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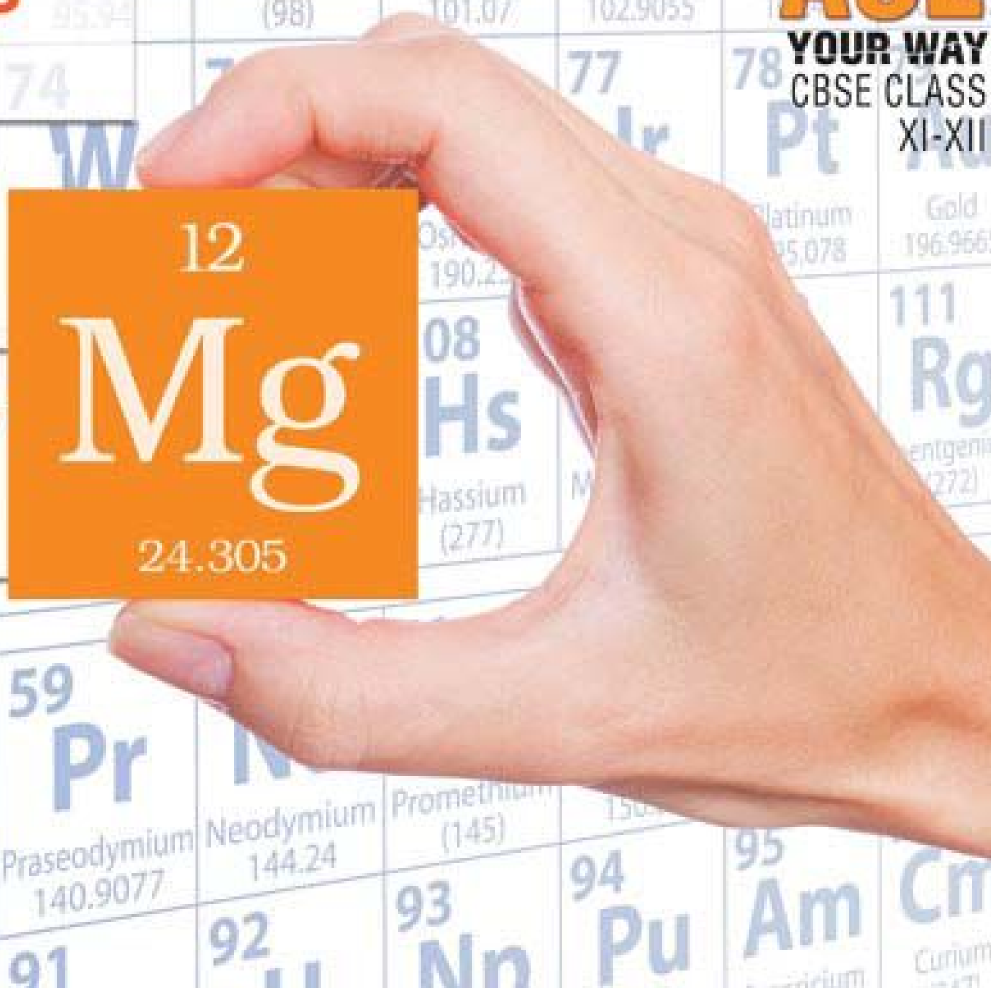

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Managing Editor
Mahabir Singh

Editor
Anil Ahlawat
(BE, MBA)

Corporate Office:
Plot 99, Sector 44 Institutional area, Gurgaon -122 003 (HR).
Tel : 0124-6601200 e-mail : info@mtg.in website : www.mtg.in

Regd. Office:
406, Taj Apartment, Near Safdarjung Hospital, New Delhi - 110029.

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NEET | JEE ESSENTIALS

Class XI

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Unit 3 STATES OF MATTER : GASES AND LIQUIDS THERMODYNAMICS

STATES OF MATTER : GASES AND LIQUIDS

EXISTENCE OF DIFFERENT STATES OF MATTER

- A substance may exist as *solid*, *liquid* or *gas* under appropriate conditions of temperature and pressure.
- A substance may also exist simultaneously in all the three states under certain specific conditions of temperature and pressure. For example, water exists as ice, water and water vapour at 0.01°C and 4.58 mm of Hg pressure. Such temperature of a substance is said to be its *triple point*.

GASEOUS STATE

- Gaseous state exists in two different forms : vapour form (exists below critical temperature) and gas form (exists above critical temperature).
- **Measurable properties of gases :**
  - Mass (S.I. unit – kg)
  - Volume (S.I. unit – m^3)
  - Temperature (S.I. unit – K)
  - Pressure (S.I. unit – Pa)

1 atm							
760 mm Hg	760 torr	76 cm Hg	14.7 psi	$101325\ N\ m^{-2}$	101325 Pa	101.325 kPa	1.01325 bar

1 bar = 0.987 atm, 1 bar = 10^2 kPa

INFO SHOTS

Mysterious new state of matter in a real material !

Researchers have just discovered the evidence of the new state known as 'quantum spin liquid' and it causes electrons to break down into smaller quasiparticles. The electrons aren't actually splitting down into smaller physical particles but the new state of matter is breaking electrons down into quasiparticles. Quasiparticles are not actually real particles, but are concepts used by physicists to explain and calculate the strange behaviour of particles. The matter itself also isn't a liquid in the traditional sense of word, but it instead refers to the fact that the quantum spins of the electrons in the material suddenly start interacting to create a disordered state, creating all kinds of strange behaviours.

Gas Laws

Gas Laws

Boyle's Law
At constant T,
$V \propto \frac{1}{P}$ or $P_1V_1 = P_2V_2$

Charles' Law
At constant P,
$V_t = V_0 + \frac{t(°C)}{273.15}V_0$ or $V \propto T$ or $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

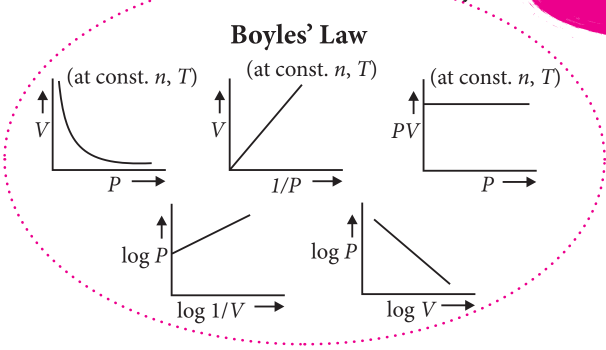
Gay-Lussac's Law
At constant V,
$P \propto T$ or $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

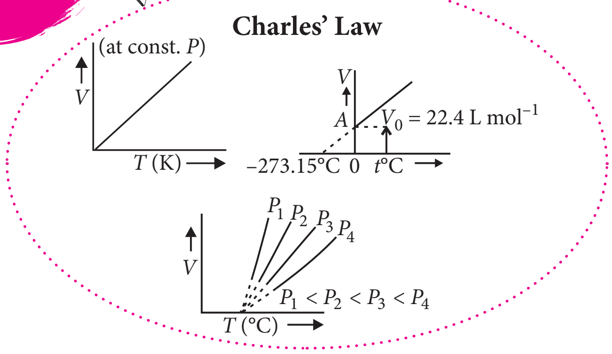
Dalton's Law of Partial Pressures
$P_{total} = p_1 + p_2 + p_3 + ... p_n$
$= (n_1 + n_2 + n_3 + ...)\frac{RT}{V}$

Avogadro's Law
At a given T and P,
$V \propto n$

Graham's Law of Diffusion
$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$

Graphical representations





Ideal gas equation : $PV = nRT$, where the constant R represents work done per degree per mole.

R (Gas constant)
- 0.0821 L atm K^{-1} mol^{-1}
- 8.314 J K^{-1} mol^{-1}
- 82.05 cm^3 atm K^{-1} mol^{-1}
- 8.314 dm^3 kPa K^{-1} mol^{-1}
- 0.083 L bar K^{-1} mol^{-1}
- 1.99 cal K^{-1} mol^{-1}
- 8.31×10^7 erg K^{-1} mol^{-1}
- 5.189×10^{19} eV K^{-1} mol^{-1}

Kinetic Theory of Gases

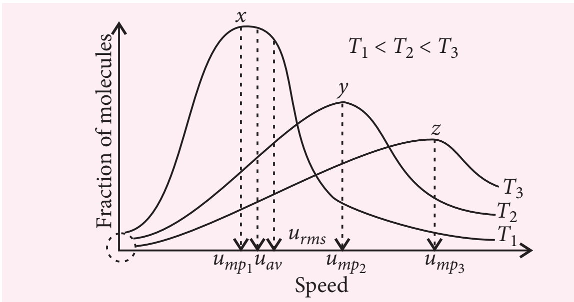
- **Kinetic gas equation :** $PV = \frac{1}{3}mNu^2$
- **Average kinetic energy per molecule :** $K.E. = \frac{3}{2}\frac{RT}{N_A} = \frac{3}{2}kT$

Molecular Speeds

Most probable speed (u_{mp})	Average speed (u_{av})	Root mean square speed (u_{rms})
$\sqrt{\frac{2RT}{M}}$	$\sqrt{\frac{8RT}{\pi M}}$	$\sqrt{\frac{3RT}{M}}$

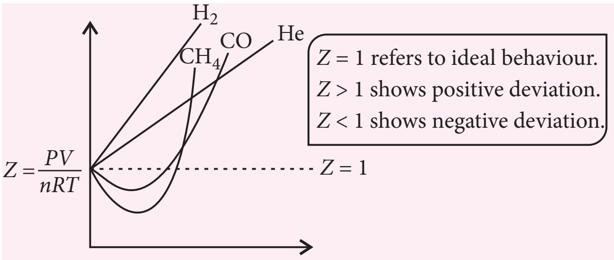
Relation between different speeds : $u_{mp} : u_{av} : u_{rms}$ = 1 : 1.128 : 1.224

Maxwell's Distribution of Speeds



Signifies that speed is never zero but it tends towards zero.

Behaviour of Real or Non-ideal Gases



where, Z is compressibility factor which measures the deviation from ideal behaviour.

- **van der Waals' Equation for real gases :**

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

where, a is the measure of the attractive forces between molecules and b is the measure of the effective size of the molecules.

- **Boyle's temperature (or Boyle point):** It is the temperature at which a real gas obeys ideal gas law over an appreciable range of pressure.

Critical Constants

- **Critical temperature (T_c):** Temperature above which a gas cannot be liquefied howsoever high the pressure may be,

$$T_c = \frac{8a}{27Rb}$$

- **Critical pressure (P_c):** Minimum pressure required to liquefy the gas at T_c.

$$P_c = \frac{a}{27b^2}$$

- **Critical volume (V_c):** Volume occupied by one mole of the gas at T_c and P_c.

$$V_c = 3b$$

LIQUID STATE

- Liquids are neither completely disordered like gases nor completely ordered like solids.

Properties of Liquids

- **Vapour pressure :** The pressure exerted by the vapour of the liquid in equilibrium with the liquid at a given temperature.

$$\log\frac{P_2}{P_1} = \frac{\Delta H}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

  - For a liquid having weaker forces of attraction, it would be higher.
  - On increasing temperature, kinetic energy of molecules increases hence, they escape into vapour readily which increases the vapour pressure.

- **Surface tension :** The force acting on the surface of liquid at right angle to any line of one centimetre length.

$$\frac{\gamma_1}{\gamma_2} = \frac{n_1 d_2}{n_2 d_1}$$

  - On increasing temperature, intermolecular forces decreases thus, surface tension decreases.

- **Viscosity :** It is the measure of resistance to flow as layers of fluid slip past one another while liquid flows.

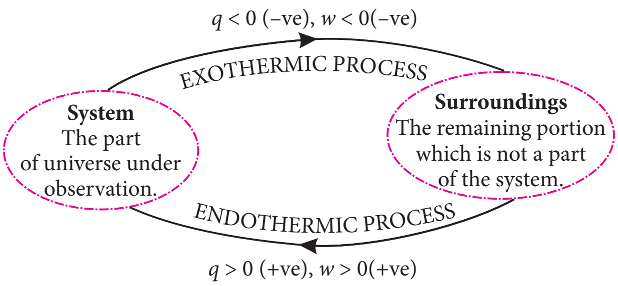
Force of friction, $F = \eta\frac{Adv}{dx}$

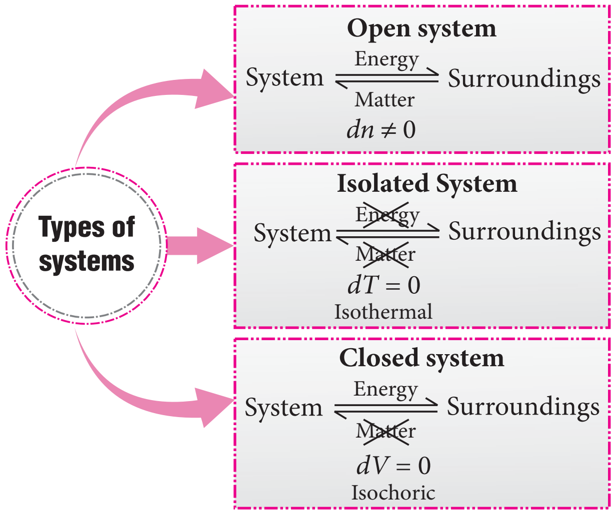
where η is a constant known as coefficient of viscosity and $\frac{dv}{dx}$ is called velocity gradient.

  - On increasing temperature, it decreases (about 2% decrease per degree rise in temperature) due to the increase in kinetic energy of molecules.

- The branch of science which deals with the study of different forms of energy and their interconversions is called *thermodynamics*.

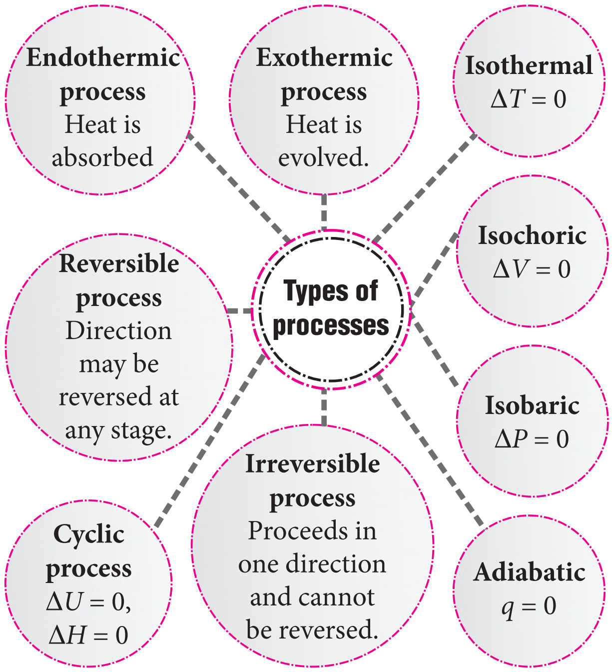
FUNDAMENTALS OF THERMODYNAMICS





Extensive	Both	Intensive
Depends on the amount of matter in the system and are additive in nature. Ratio of two extensive property is always intensive. Examples include size, mass, length, shape, volume, entropy, enthalpy, gibbs free energy, internal energy, etc.	Can be observed, changed, or measured without altering the identity of the system. Used to observe and describe matter.	Depends only on the nature of the matter in the system and are non-additive in nature. Examples include density, temperature, pressure, molar entropy, surface tension, refractive index, viscosity, specific heat, etc.

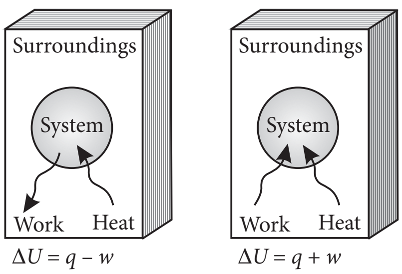
- **State functions :** Properties which are used to define a particular thermodynamic state and are independent of the path by which the state is attained are called *state functions*. *e.g.*, pressure, mass composition, volume, temperature, internal energy, entropy, Gibbs free energy, etc.
- **Path functions :** Variables whose values depend upon the path followed by the system in attaining that state are known as *path functions*.



THERMODYNAMIC LAWS

- **0^{th} Law :** If the two thermodynamic systems are in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.
- **1^{st} Law :** Total energy of the universe remains constant, although it may undergo transformation from one form to another.
- **2^{nd} Law :** All spontaneous processes are thermodynamically irreversible.
- **3^{rd} Law :** At absolute zero temperature, the entropy of a perfectly crystalline substance is taken as zero.

FIRST LAW OF THERMODYNAMICS



- Some important thermodynamic quantities :

Thermodynamic quantities

Internal energy

$\Delta U = U_2 - U_1$

$\Delta U = +\text{ve}\ (U_2 > U_1)$

$\Delta U = -\text{ve}\ (U_2 < U_1)$

$\Delta U = 0$ (cyclic process)

$\Delta U = q_v$ (at constant volume)

$$\Delta U = Q \times \Delta t \times \frac{M}{m}$$

where Q = heat capacity of the calorimeter,
Δt = rise in temperature
m = mass of the substance
M = molecular mass of the substance

Heat capacity

$$C = \frac{q}{\Delta T}$$

$$C_v = \left(\frac{dq}{dT}\right)_v = \left(\frac{\partial U}{\partial T}\right)_v$$

$$C_p = \left(\frac{\partial q}{dT}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p$$

Heat

Heat evolved or absorbed, $\Delta q = ms\Delta t$
q = +ve (Heat absorbed by the system)
q = –ve (Heat evolved from the system)

Work

$$w_{\text{irr}} = -P_{\text{ext}}\,\Delta V$$

$$w_{\text{rev}} = -2.303nRT\log\frac{V_2}{V_1} = -2.303nRT\log\frac{P_1}{P_2}$$

Enthalpy

$\Delta H = \Delta U + P\Delta V$

$\Delta H = q_p$ (at constant pressure)

In case of solids and liquids,
$\Delta H \approx \Delta U$ as $P\Delta V \approx 0$

In case of gases,
$\Delta H = \Delta U + \Delta n_g RT$

Specific heat capacity

$$C_s = \frac{C}{m} \text{ in JK}^{-1}\text{ g}^{-1}$$

Molar heat capacity

$$C_m = \frac{C}{n} \text{ in JK}^{-1}\text{ mol}^{-1}$$

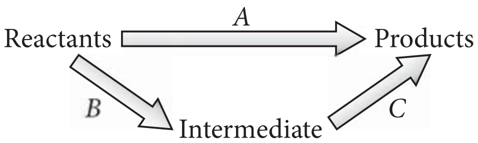
Clausius-Clapeyron Equation

$$\log\frac{P_2}{P_1} = \frac{\Delta H_{vap}}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

ΔH_{vap} = Molar heat of vaporisation

Hess's Law

- Hess's law states that, if a reaction can take place by more than one route and the initial and final conditions are same, the total enthalpy change is the same.

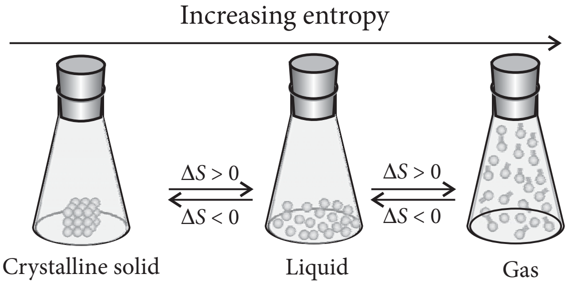


$\Delta H_A = \Delta H_B + \Delta H_C$

- **Applications :** Heat changes for those reactions can be calculated whose experimental determination is not possible.

Second Law of Thermodynamics

- **Entropy :** Measure of degree of disorder or randomness of the system.



- $\Delta S = \Sigma S_{(\text{products})} - \Sigma S_{(\text{reactants})}$

- $\Delta S = \dfrac{q_{rev}}{T}$

- $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$

- $\Delta_{\text{fus}} S = \dfrac{\Delta_{\text{fus}} H}{T_m}$, $\Delta_{\text{vap}} S = \dfrac{\Delta_{\text{vap}} H}{T_b}$,

$$\Delta_{\text{sub}} S = \frac{\Delta_{\text{sub}} H}{T}$$

Entropy changes for various types of processes :

Process	ΔS
Isothermal reversible expansion of an ideal gas	$nR\ln\left(\frac{V_2}{V_1}\right)$
Adiabatic reversible expansion	0 as $q = 0$ (isoentropic)
Adiabatic free expansion	$\neq 0$
Isobaric process	$C_p \ln\frac{T_2}{T_1}$
Isochoric process	$C_v \ln\frac{T_2}{T_1}$

Second law of thermodynamics : It states that the entropy of the universe is continuously increasing or heat cannot flow on its own from colder to hotter region.

- For a reversible process, $\Delta S_{sys} + \Delta S_{surr} = 0$
- For an irreversible process, $\Delta S_{sys} + \Delta S_{surr} > 0$

GIBBS FREE ENERGY

Gibbs free energy : It is the maximum amount of energy available to system to convert into useful work during the process.

- $G = H - TS$
- $\Delta G = \Delta H - T\Delta S$ (Gibbs–Helmholtz equation)
- $\Delta G° = -nFE°_{cell}$
- $\Delta G° = \Sigma G°_{f\,(products)} - \Sigma G°_{f\,(reactants)}$
- $\Delta G° = -2.303\ RT \log K_{eq}$

Gibbs free energy and spontaneity :

ΔH	ΔS	$\Delta G = \Delta H - T\Delta S$	Reaction characteristic
–	+	Always –ve	Spontaneous at all temperatures
+	–	Always +ve	Non-spontaneous at all temperatures
–	–	–ve at low temperature and +ve at high temperature	Spontaneous at low temperature Non-spontaneous at high temperature
+	+	+ve at low temperature and –ve at high temperature	Non-spontaneous at low temperature Spontaneous at high temperature

THIRD LAW OF THERMODYNAMICS

For solid at temperature, T K

$$\Delta S = S_{T\,K} - S_{0\,K} = \int_0^T \frac{C_p dT}{T} = \int_0^T C_p d\ln T$$

From third law of thermodynamics, $S_{0\,K} = 0$

$S_{TK} = C_p \ln T = 2.303\ C_p \log T$

For liquids and gases, the absolute entropy at a given temperature T is given by the expression,

$$S = \int_0^{T_f} \frac{C_{p(s)}dT}{T} + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_b} \frac{C_{p(l)}dT}{T} + \frac{\Delta H_{vap}}{T_b} + \int_{T_b}^{T} \frac{C_{p(g)}dT}{T}$$

INFO SHOTS

Diamonds help generate new record for static pressure for study !

In 2016, a method is divised for achieving static pressures vastly higher than any previously reached. Traditionally, a diamond anvil cell works like a vice that squeezes the sample between two single-crystal diamonds to produce extreme pressure. In the new device, a miniscule ball of nano-crystalline diamonds sits atop each single-crystal diamond. As the diamonds are squeezed together, the load is transferred from the larger diamond to the nano-ball. This causes the nano-diamond balls to compress and actually get harder, allowing them to both generate and withstand extreme pressures.

Extraordinary things happen to ordinary materials when they are subjected to very high pressure and temperature. Sodium, a conductive metal in normal conditions, becomes a transparent insulator; gaseous hydrogen becomes a solid.

SPEED PRACTICE

1. The volume of the average adult human lungs when expanded is about 6 litres at 98.4°F. If the pressure of oxygen in inhaled air is 168 mm of Hg then the mass of O_2 required to occupy the lungs at 98.4°F is
(a) 2.67 g (b) 1.06 g (c) 1.67 g (d) 3.76 g

2. Two litres of N_2 at 0°C and 5 atm pressure are expanded isothermally against a constant external pressure of 1 atm until the pressure of gas reaches 1 atm. Assuming gas to be ideal, the work of expansion is
(a) 801.10 J (b) –810.40 J (c) 0.801 J (d) 108.10 J

3. Two gas containers with volumes 0.1 L and 1 L respectively are connected by a tube of negligible volume and contains air at a pressure of 1000 mm of Hg at 0°C. If the temperature of smaller container is raised to 100°C, the volume of air measured at 0°C and 760 mm of Hg that will pass from it to larger container will be
(a) 30 mL (b) 42.3 mL (c) 32.9 mL (d) 12 mL

4. One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings (ΔS_{surr}) in J K^{-1} is (1 L atm = 101.3 J)
(a) 5.763 (b) 1.013 (c) –1.013 (d) –5.763
(JEE Advanced 2016)

5. A mixture of C_2H_6 and C_2H_4 occupies 40 litres at 1 atm and at 400 K. The mixture reacts completely with 130 g of O_2 to produce CO_2 and H_2O. Assuming ideal gas behaviour, the mole fractions of C_2H_4 in the mixture is
(a) 0.33 (b) 0.67 (c) 0.43 (d) 0.57

6. The standard molar heats of formation of ethane, carbon dioxide and water are – 21.1, – 94.1 and – 68.3 kcal respectively. The standard molar heat of combustion of ethane (in kcal) is
(a) 372.0 (b) 472.0 (c) – 472.0 (d) – 372.0

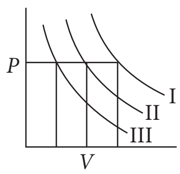
7. The diffusion coefficient of an ideal gas is proportional to its mean free path and mean speed. If absolute temperature of the gas is increased 4 times and pressure is increased 2 times, the diffusion coefficient increases x times. The value of x is
(a) 1/4 (b) 1/2 (c) 4 (d) 2

8. Only N_2 and CO_2 gases remain after 15.5 g of carbon is treated with 25 litres of air at 25°C and 5.5 atm pressure. Assuming composition of air : O_2 – 19%, N_2 – 80% and CO_2 – 1% (by volume), the total heat evolved under constant pressure is

$$\left(\begin{array}{l} C + O_2 \rightarrow CO_2; \quad \Delta H = -94.05 \text{ kcal/mole} \\ C + \frac{1}{2}O_2 \rightarrow CO; \quad \Delta H = -26.41 \text{ kcal/mole} \end{array}\right)$$

(a) – 91.2 kcal (b) 91.2 kcal
(c) 90.2 kcal (d) 93.2 kcal

9. I, II, and III are three isotherms respectively at T_1, T_2, and T_3. Temperature will be in order
(a) $T_1 = T_2 = T_3$ (b) $T_1 < T_2 < T_3$
(c) $T_1 > T_2 > T_3$ (d) $T_1 > T_2 = T_3$

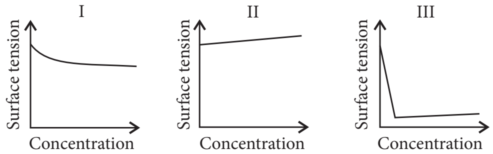


10. A flask containing 12 g of a gas of relative molecular mass 120 at a pressure of 100 atm was evacuated by means of a pump until the pressure was 0.01 atm. Which of the following is the best estimate of the number of molecules left in the flask ($N_0 = 6 \times 10^{23}$ mol^{-1})?
(a) 6×10^{19} (b) 6×10^{18}
(c) 6×10^{17} (d) 6×10^{13}

11. A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 to 2.50 dm^3. The enthalpy change in this process in J/kJ is ($C_{v,m}$ for argon is 12.48 JK^{-1} mol^{-1}).
(a) – 114.52 (b) 115.62 (c) +114.52 (d) –115.62

12. The lattice energy of solid NaCl is 180 kcal mol^{-1}. The dissolution of the solid in H_2O is endothermic to the extent of 1.0 kcal mol^{-1}. If the hydration energies of Na^+ and Cl^- ions are in the ratio of 6 : 5, the enthalpy of hydration of sodium ion in kcal mol^{-1} is
(a) – 85 (b) – 98 (c) + 82 (d) + 100

13. The qualitative sketches I, II and III given below show the variation of surface tension with molar concentration of three different aqueous solutions KCl, CH_3OH and $CH_3(CH_2)_{11}OSO_3^-Na^+$ at room temperature. The correct assignment of the sketches is



	I	II	III
(a)	KCl	CH_3OH	$CH_3(CH_2)_{11}OSO_3^-Na^+$
(b)	$CH_3(CH_2)_{11}$ $OSO_3^-Na^+$	CH_3OH	KCl
(c)	KCl	$CH_3(CH_2)_{11}$ $OSO_3^-Na^+$	CH_3OH
(d)	CH_3OH	KCl	$CH_3(CH_2)_{11}OSO_3^-Na^+$

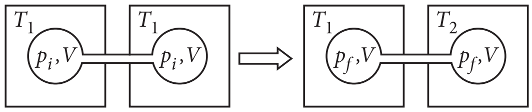
(JEE Advanced 2016)

14. Calculate the entropy change when 1 kg of water is heated from 27°C to 200°C forming super-heated steam under constant pressure. Given specific heat of water = 4180 J/ kg/K and specific heat of steam = 1670 + 0.49 T J/kg/K (where T is absolute temperature) and latent heat of vaporisation = 23×10^5 J/kg .
(a) 7522.5 J (b) 75.22 J (c) 7.522 J (d) 445.2 J

15. For two gases, A and B with molecular masses M_A and M_B, it is observed that at a certain temperature T the mean velocity of A is equal to the root mean square velocity of B. Thus, the mean velocity of A can be made equal to the mean velocity of B, if
(a) A is at temperature T, and B at T_2, $T_2 > T$
(b) A is lowered to a temperature $T_2 < T$ while B is at T
(c) both A and B are raised to a higher temperature
(d) both A and B are placed at lower temperature.

16. A solution of 200 mL of 1 M KOH is added to 200 mL of 1 M HCl and the mixture is well shaken. The rise in temperature (T_1) is noted during this process. The experiment is repeated by using 100 mL of each solution and increase in temperature T_2 is again noted. Which of the following is correct?
(a) $T_1 = T_2$
(b) T_2 is twice as large as T_1
(c) T_1 is twice as large as T_2
(d) T_1 is four times as large as T_2

17. Two closed bulbs of equal volume (V) containing an ideal gas initially at pressure p_i and temperature T_1 are connected through a narrow tube of negligible volume as shown in the figure below. The temperature of one of the bulbs is then raised to T_2. The final pressure p_f is



(a) $p_i\left(\dfrac{T_1T_2}{T_1+T_2}\right)$ (b) $2p_i\left(\dfrac{T_1}{T_1+T_2}\right)$
(c) $2p_i\left(\dfrac{T_2}{T_1+T_2}\right)$ (d) $2p_i\left(\dfrac{T_1T_2}{T_1+T_2}\right)$

(JEE Main 2016)

18. An ideal gas has a specific heat at constant pressure $C_p = (5/2)R$. The gas is kept in a closed vessel of volume 0.0083 m^3, at a temperature of 300 K and pressure 1.6×10^6 N/m^2. An amount of 2.49×10^4 J of energy is supplied to the gas. The final temperature of the gas in kelvin is
(a) 575 K (b) 675 K (c) 579 K (d) 765 K

19. 22 g solid CO_2 or dry ice is enclosed in a properly closed bottle of one litre. If the temperature of bottle is raised to 25°C to evaporate all the CO_2, the pressure in bottle is
(a) 13.23 atm (b) 12.23 atm
(c) 11.23 atm (d) 14.23 atm

20. For complete combustion of ethanol,
$C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$
the amount of heat produced as measured in bomb calorimeter, is 1364.47 kJ mol^{-1} at 25°C. The enthalpy of combustion, $\Delta_{comb}H$ (in kJ mol^{-1}) for the reaction will be (R = 8.314 kJ mol^{-1})
(a) –1366.95 (b) –1361.95
(c) –1460.50 (d) –1350.50

21. Equal moles of hydrogen and oxygen gases are placed in a container with a pin-hole through which both can escape. What fraction of the oxygen escapes in the time required for one-half of the hydrogen to escape?
(a) 3/8 (b) 1/2 (c) 1/8 (d) 1/4

(NEET 2016)

22. At 298 K, the enthalpy of solution of solid magnesium sulphate is – 91.21 kJ mol^{-1} and that of hydrated magnesium sulphate is 13.81 kJ mol^{-1}. The heat of hydration of solid magnesium sulphate is
(a) – 91.21 (b) – 105.02 (c) + 105.02 (d) + 91.21

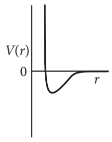
23. Gases X, Y, Z, P and Q have the van der Waals' constants a and b (in CGS units) as shown below:

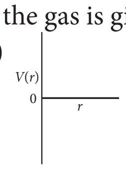
Gases	X	Y	Z	P	Q
a	6	6	20	0.05	30
b	0.025	0.15	0.1	0.02	0.2

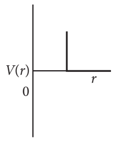
The gas with the highest critical temperature is
(a) P (b) Q (c) Y (d) X

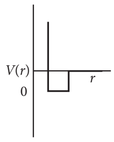
24. A gas is heated in such a way so that its pressure and volume both become double. Again by lowering temperature, one fourth of initial number of moles of air has been taken in, to maintain the double volume and pressure. By what fraction, the temperature must have been raised finally?
(a) 1/5 (b) 4/5 (c) 16/5 (d) 8/5

25. One mole of a monoatomic real gas satisfies the equation $p(V - b) = RT$ where b is a constant. The relationship of interatomic potential $V(r)$ and interatomic distance r for the gas is given by

(a)


(b)


(c)


(d)


(JEE Advanced 2015)

26. A gas expands from 3 dm^3 to 5 dm^3 against a constant pressure of 3 atm. The work done during expansion is used to heat 10 moles of water at temperature 290 K. Calculate final temperature of water. Specific heat of water = 4.184 J g^{-1} K^{-1}.
(a) 281 K (b) 290.81 K (c) 299.8 K (d) 288 K

27. The standard heats of formation for $CCl_{4(g)}$, $H_2O_{(g)}$, $CO_{2(g)}$ and $HCl_{(g)}$ are –25.5, –57.8, –94.1 and –22.1 kcal repectively. Calculate $\Delta H_{(298\text{ K})}$ (in kcal) for the reaction : $CCl_{4(g)} + 2H_2O_{(g)} \rightarrow CO_{2(g)} + 4HCl_{(g)}$
(a) –41.4 (b) 41.4 (c) 4.14 (d) 414

28. For the process, $H_2O_{(l)} \rightarrow H_2O_{(g)}$ at $T = 100°C$ and $P = 1$ atm, the correct choice is
(a) $\Delta S_{system} > 0$ and $\Delta S_{surroundings} > 0$
(b) $\Delta S_{system} > 0$ and $\Delta S_{surroundings} < 0$
(c) $\Delta S_{system} < 0$ and $\Delta S_{surroundings} > 0$
(d) $\Delta S_{system} < 0$ and $\Delta S_{surroundings} < 0$

(JEE Advanced 2014)

29. A compound exists in the gaseous phase both as monomer (A) and dimer (A_2). The molecular weight of A is 48. In an experiment 96 g of the compound was confined in a vessel of volume 33.6 litre and heated to 273°C. The pressure developed if the compound exists as dimer to the extent of 50% by weight under these conditions is
(a) 2 atm (b) 4 atm (c) 3 atm (d) 5 atm

30. One mole of nitrogen gas at 0.8 atm takes 38 seconds to diffuse through a pinhole, whearas one mole of an unknown compound of xenon with fluorine at 1.6 atm takes 57 seconds to diffuse through the same hole. Calculate the molecular mass of the compound.
(a) 252 (b) 525 (c) 262 (d) 380

SOLUTIONS

1. (c) : 98.4°F can be converted to °C as

$$\frac{°F - 32}{9} = \frac{°C}{5} \Rightarrow \frac{98.4 - 32}{9} = \frac{°C}{5}$$

$\therefore$ $T = 36.88°C$ or 309.88 K

Thus using, $PV = \dfrac{w}{M}RT$

$$\frac{168}{760} \times 6 = \frac{w}{32} \times 0.0821 \times 309.88 \Rightarrow w = 1.67 \text{ g}$$

2. (b)

3. (c) : Moles present initially in 1 L container

$$n_1 = \frac{PV}{RT} = \frac{1000 \times 1}{760 \times 0.0821 \times 273} = 5.87 \times 10^{-2}$$

Moles present initially in 0.1 L container

$$n_2 = \frac{PV}{RT} = \frac{1000 \times 0.1}{760 \times 0.0821 \times 273} = 5.87 \times 10^{-3}$$

$\therefore n_1 + n_2 = 5.87 \times 10^{-2} + 5.87 \times 10^{-3} = 6.46 \times 10^{-2}$

Also, on heating the vessel of 0.1 L to 373 K, let 'n' moles remain in it. As pressure will remain same, so nRT/V is constant in both the containers.

$$\therefore \frac{n \times 373}{0.1} = \frac{(6.46 \times 10^{-2} - n) \times 273}{1} \Rightarrow n = 4.40 \times 10^{-3}$$

i.e., Moles left in 0.1 litre container after heating $= 4.40 \times 10^{-3}$

$\therefore$ Moles moved from 0.1 L to 1 L vessel
$= 5.87 \times 10^{-3} - 4.40 \times 10^{-3} = 1.47 \times 10^{-3}$

$\therefore$ Volume of air moved at 0°C and 760 mm

$$V = \frac{nRT}{P} = \frac{1.47 \times 10^{-3} \times 0.0821 \times 273}{1} = 32.9 \text{ mL}$$

4. (c)

5. (a) : Let the number of moles of C_2H_6 and C_2H_4 be n_1 and n_2 respectively. Applying ideal gas equation, $PV = nRT$.

$1 \times 40 = (n_1 + n_2) \times 0.0821 \times 400$ ...(i)

$C_2H_6 + C_2H_4 + O_2 \rightarrow CO_2 + H_2O$

For C, $2n_1 + 2n_2$ = Moles of CO_2 ...(ii)

For H, $6n_1 + 4n_2 = 2 \times$ Moles of H_2O ...(iii)

For O, $2 \times \dfrac{130}{32} = 2 \times$ Moles of CO_2 + Moles of H_2O ...(iv)

From equations (ii), (iii) and (iv) we get,

$$7n_1 + 6n_2 = \frac{260}{32} \quad ...(v)$$

Solving equations (i) and (v) we get,

$n_1 = 0.8168$; $n_2 = 0.4012$

$\therefore$ Mole fraction of $C_2H_6 = \dfrac{0.8168}{0.8168 + 0.4012} = 0.67$

Mole fraction of $C_2H_4 = 1 - 0.67 = 0.33$

6. (d)

7. (c) : Diffusion coefficient $\propto \lambda\, C_{mean}$

$\lambda \propto \dfrac{T}{P}$ and $C_{mean} \propto \sqrt{T}$

Diffusion coefficient $\propto \dfrac{T}{P}\sqrt{T} \propto \dfrac{T^{3/2}}{P}$

If T is increased four times and pressure is increased two times diffusion coefficient will become 4 times.

8. (a) : Moles of C $= \dfrac{15.5}{12} = 1.292$

Moles of $O_2 = \dfrac{PV}{RT} = \dfrac{5.5 \times (0.19 \times 25)}{0.0821 \times 298} = 1.068$

$$\underset{x \text{ mole}}{C} + O_2 \rightarrow \underset{x \text{ mole}}{CO_2}$$

$$\underset{(1.292-x)\text{ moles}}{C} + 1/2O_2 \rightarrow \underset{(1.292-x)\text{ moles}}{CO}$$

As O_2 is fully consumed,

Number of moles of O before reaction = Number of moles of O after reaction = Moles of O in CO_2 + Moles of O in CO

or $2 \times 1.068 = 2x + (1.292 - x) \Rightarrow x = 0.844$

Moles of $CO_2 = 0.844$; Moles of CO $= 1.292 - 0.844 = 0.448$

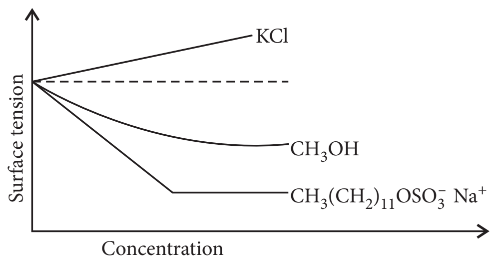
Total heat evolved $= 0.844\,(-94.05) + 0.448\,(-26.41)$

$= -91.2$ kcal

9. (c) : Draw a line at constant P parallel to volume axis. Take volume corresponding to each temperature. From volume axis, $V_1 > V_2 > V_3$ Hence, $T_1 > T_2 > T_3$

10. (b) **11. (a)** **12. (b)**

13. (d) :



KCl curve : Increase of surface tension for inorganic salts.

CH_3OH curve : Decrease of surface tension progressively for alcohols.

$CH_3(CH_2)_{11}OSO_3^-Na^+$ curve : Decrease of surface tension before CMC (Critical Micelle Concentration) and then almost unchanged.

14. (a) : $\Delta S = 2.303n \times C_p \times \log\dfrac{T_2}{T_1}$

ΔS for heating water from 27°C to 100°C,

$$\Delta S = 2.303 \times \frac{1000}{18} \times \frac{4180 \times 18}{1000} \log\frac{373}{300} = 910.55\text{ J}$$

ΔS for heating 1 kg H_2O to 1 kg steam at 100°C,

$$\Delta S = \frac{\Delta H_v}{T} = \frac{23 \times 10^5}{373} = 6166.21\text{ J}$$

ΔS for heating 1 kg steam from 373 to 473 K,

$$\Delta S = \int_{373}^{473} \frac{nC_p \cdot dT}{T} = m\int_{373}^{473} \frac{(1670 - 0.49T)}{T}\, dT$$

$= 396.73 + 49 = 445.73$ J, where m = mass in kg

Total $\Delta S = 910.55 + 6166.21 + 445.73 = 7522.50$ J

15. (b) : $u_{av(A)} = \sqrt{8RT/\pi M_A}$; $u_{rms(B)} = \sqrt{3RT/\pi M_B}$

$\therefore \dfrac{8}{3\pi} = \dfrac{M_A}{M_B}$

For $u_{av(A)} = \sqrt{\dfrac{8RT_2}{\pi M_A}}$; $u_{av(B)} = \sqrt{\dfrac{8RT}{\pi M_B}}$

$\dfrac{T_2}{T} = \dfrac{M_A}{M_B} = \dfrac{8}{3\pi}$ $\therefore T_2 = \dfrac{8}{3\pi} \cdot T$ or $T_2 < T$

16. (a) : Heat produced by 200 meq. of mixture $= \dfrac{-13.7 \times 200}{1000}$ kcal. This is used to raise the temperature of 400 mL solution say by T_1.

Similarly, heat produced by 100 meq. of mixture $= \dfrac{-13.7 \times 100}{1000}$ kcal. This is used to raise the temperature of 200 mL solution say by T_2

It is evident that $T_1 = T_2$

17. (c)

18. (b) : Let n moles of gas be present

$$\therefore \quad n = \frac{PV}{RT} = \frac{1.6 \times 10^6 \times 0.0083}{8.3 \times 300} = 5.33$$

Given, $C_p = \dfrac{5}{2}R$

$$\therefore \quad C_v = \frac{5}{2}R - R = \frac{3}{2}R = \frac{3}{2} \times 8.3 = 12.45\text{ J mol}^{-1}\text{K}^{-1}$$

Heat supplied at constant volume $= n \times C_v \times \Delta T$

$\Rightarrow$ 2.49×10^4 J $= 5.33 \times 12.45$ J mol^{-1} K^{-1} $\times \Delta T$

$\Rightarrow$ $\Delta T = 375$ K

$\therefore$ Final temperature $= 300 + 375 = 675$ K

19. (a) : $w = 22$ g; $V = 1$ litre, $T = 298$ K

$$PV = \frac{w}{M}RT \text{ (for } CO_2\text{)}$$

$$P \times 1 = \frac{22}{44} \times 0.0821 \times 298 \;\therefore\; P_{CO_2} = 12.23 \text{ atm}$$

$\therefore\; P_{\text{in bottle}} = P_{CO_2} + \text{atm pressure} = 12.23 + 1 = 13.23 \text{ atm}$

20. (a) : $C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$

Bomb calorimeter gives ΔU of the reaction.

$\Delta H = \Delta U + \Delta n_g RT$

$\Delta U = -1364.47 \text{ kJ mol}^{-1}; \Delta n_g = -1$

$$\Delta H = -1364.47 - \frac{1 \times 8.314 \times 298}{1000} \Rightarrow -1366.93 \text{ kJ mol}^{-1}$$

21. (c) : Let the number of moles of each gas $= x$

Fraction of hydrogen escaped $= \frac{1}{2}x$

$$\frac{r_{O_2}}{r_{H_2}} = \sqrt{\frac{M_{H_2}}{M_{O_2}}} \Rightarrow \frac{n_{O_2}/t}{\frac{x}{2}/t} = \sqrt{\frac{2}{32}} = \sqrt{\frac{1}{16}} = \frac{1}{4}$$

$$\Rightarrow \frac{n_{O_2}/t}{\frac{x}{2}/t} = \frac{1}{4} \Rightarrow n_{O_2} = \frac{1}{8}x$$

Hence, fraction of oxygen escaped $= \frac{1}{8}$

22. (b) : Given

(i) $MgSO_{4(s)} + \underset{\text{Excess}}{7H_2O} \longrightarrow MgSO_4 \cdot 7H_2O_{(aq)};$ $\Delta_{sol}H_1 = -91.21 \text{ kJ mol}^{-1}$

(ii) $MgSO_4{\cdot}7H_2O_{(s)} + \underset{\text{(Excess)}}{H_2O} \rightarrow MgSO_4{\cdot}7H_2O_{(aq)};$ $\Delta_{sol}H_2 = 13.81 \text{ kJ mol}^{-1}$

Eq. (i), involves the following two steps :

$MgSO_{4(s)} + 7H_2O \rightarrow MgSO_4{\cdot}7H_2O_{(s)}; \Delta_{hyd}H_3 = ?$

$MgSO_4{\cdot}7H_2O_{(s)} + \underset{\text{(Excess)}}{H_2O} \rightarrow MgSO_4{\cdot}7\,H_2O_{(aq)};$ $\Delta_{sol}H_2 = 13.81 \text{ kJ mol}^{-1}$

Thus, $\Delta_{hyd}H_3 = \Delta_{sol}H_1 - \Delta_{sol}H_2 = -91.21 - 13.81$
$= -105.02 \text{ kJ mol}^{-1}$

23. (d) : Critical temperature, $T_c = \frac{8a}{27Rb}$

Greater the value of $\left(\frac{a}{b}\right)$, more is the critical temperature of gas.

Gas X, $\frac{a}{b} = \frac{6}{0.025} = 240$; Gas Y, $\frac{a}{b} = \frac{6}{0.150} = 40$;

Gas Z, $\frac{a}{b} = \frac{20}{0.1} = 200$; Gas P, $\frac{a}{b} = \frac{0.05}{0.02} = 2.5$;

Gas Q, $\frac{a}{b} = \frac{30}{0.2} = 150$

Therefore, gas X will have the highest critical temperature.

24. (c) : $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \Rightarrow \frac{P_1V_1}{T_1} = \frac{2P_1 \times 2V_1}{T_2} \Rightarrow T_2 = 4T_1$

When air has been taken in and P, V remain constant; $n_1{\cdot}4T_1 = n_2{\cdot}T_2$

Initial no. of moles $= n$

$n_1 = n$ and $n_2 = n + \frac{1}{4}n = \frac{5}{4}n$

$\text{Total} = n_1 + \frac{n_1}{4} = \frac{5}{4}n_1$

$\therefore\; n \cdot 4T_1 = \frac{5}{4}n \cdot T_2 \Rightarrow T_2 = \frac{16}{5}T_1$

25. (c)

26. (b) : Work is done against constant P hence, it is irreversible.

$\Delta V = 5 - 3 = 2 \text{ dm}^3 = 2$ litre ; $P = 3$ atm

$\therefore\; w_{irr} = -P{\cdot}\Delta V = -3 \times 2$ L atm

$$= -\frac{6 \times 4.184 \times 1.987}{0.0821} \text{ joule} = -607.57 \text{ joule}$$

Now, this work is used for heating water

$w = n \times C \times \Delta T$

$607.57 = 10 \times 4.184 \times 18 \times \Delta T$

$\therefore\; \Delta T = 0.81$

$\therefore$ Final temperature $= T_1 + \Delta T = 290 + 0.81$
$= 290.81$ K

27. (a) : At 298 K, ΔH values are $\Delta H°$, *i.e.*, standard heat of formation. For

$CCl_{4(g)} + 2H_2O_{(g)} \rightarrow CO_{2(g)} + 4HCl_{(g)};\quad \Delta H° = ?$

$\Delta H°_{\text{Reaction}} = \Delta H°_{CO_2} + 4 \times \Delta H°_{HCl} - \Delta H°_{CCl_4} - 2 \times \Delta H°_{H_2O}$

$= -94.1 + 4 \times (-22.1) - (-25.5) - 2 \times (-57.8) = -41.4$ kcal

28. (b)

29. (a) : Since, A and A_2 are two states in gaseous phase having their weight ratio 50%, *i.e.*, 1:1

$\therefore$ Moles of $A = \frac{96}{2} \times \frac{1}{48} = 1$; Moles of $A_2 = \frac{96}{2} \times \frac{1}{96} = \frac{1}{2}$

$\therefore$ Total moles of A and A_2 are $= 1 + \frac{1}{2} = \frac{3}{2}$

$PV = nRT$

$$P \times 33.6 = \frac{3}{2} \times 0.0821 \times 546 = 2 \text{ atm}$$

30. (a) : $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \times \frac{P_1}{P_2}$ or $\frac{n_1}{t_1} \times \frac{t_2}{n_2} = \sqrt{\frac{M_2}{M_1}} \times \frac{P_1}{P_2}$

or $\frac{1}{38} \times \frac{57}{1} = \sqrt{\left(\frac{M_{gas}}{28}\right)} \times \frac{0.8}{1.6}$

$$\therefore\; M_{gas} = \left[\frac{57}{38} \times \frac{1.6}{0.8}\right]^2 \times 28 \Rightarrow M_{gas} = 252$$

EXAMINER'S MIND CLASS XI

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XI. This year JEE (Main & Advanced)/NEET/AIIMS have drawn their papers heavily from NCERT books.

Section - I	Q. 1 to 10 Only One Option Correct Type MCQs.
Section - II	Q. 11 to 13 More than One Options Correct Type MCQs.
Section - III	Q. 14 to 17 Paragraph Type MCQs having Only One Option Correct.
Section - IV	Q. 18 & 19 Matching List Type MCQs having Only One Option Correct.
Section - V	Q. 20 to 22 Assertion Reason Type MCQs having Only One Option Correct. Mark the correct choice as : (a) If both assertion and reason are true and reason is the correct explanation of assertion. (b) If both assertion and reason are true but reason is not the correct explanation of assertion. (c) If assertion is true but reason is false. (d) If both assertion and reason are false.
Section - VI	Q. 23 to 25 Integer Value Correct Type Questions having Single Digit Integer Answer, ranging from 0 to 9 (both inclusive).

CHEMICAL BONDING AND MOLECULAR STRUCTURE

SECTION - I

Only One Option Correct Type

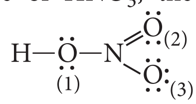
1. According to Fajan's rules, ionic bonds are formed when
(a) cations have low positive charge, large size and anions have large size.
(b) cations have low positive charge and small size
(c) cations have high positive charge and large size
(d) cations have low positive charge, large size and anions have small size.

2. Consider two elements with atomic number 37 and 53, the bond between their atoms is
(a) covalent (b) ionic
(c) coordinate (d) metallic.

3. The maximum number of 90° angles between bond pair-bond pair of electrons is observed in hybridisation
(a) dsp^2 (b) sp^3d (c) dsp^3 (d) sp^3d^2

4. Zeise's salt contains which type of bonds?
(a) Ionic bonds (b) Hydrogen bonds
(c) Ionic and covalent bonds
(d) Ionic, covalent and coordinate bonds.

5. In the following Lewis structure of HNO_3, the formal charge on O_3 atom is

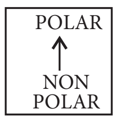


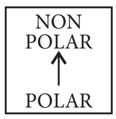
(a) 0 (b) −1 (c) −2 (d) +1

6. If the climbing of water droplets is made to occur on a coated microscope slide, the slide would have to be coated in which of the following way ?

(a)


(b)


(c)


(d)


7. If the electronegativity difference between two atoms *A* and *B* is 2.0, then the percentage of ionic character in the molecule is
(a) 54% (b) 46% (c) 23% (d) 72%

8. The bond angles of NH_3, NH_4^+ and NH_2^- are in the order
(a) $NH_2^- > NH_3 > NH_4^+$ (b) $NH_4^+ > NH_3 > NH_2^-$
(c) $NH_3 > NH_2^- > NH_4^+$ (d) $NH_3 > NH_4^+ > NH_2^-$

9. In the anion $HCOO^-$ the two carbon-oxygen bonds are found to be of equal length. What is the reason for it?
(a) Electronic orbitals of carbon atoms are hybridised.
(b) The C=O bond is weaker than C—O bond.
(c) The anion $HCOO^-$ has two resonating structures.
(d) The anion is obtained by removal of a proton from the acid molecule.

10. Carbon suboxide (C_3O_2) has been recently shown as a component of the atmosphere of venus. Which of the following formulation represents the correct ground state Lewis structure for carbon suboxide?
(a) : O : C:: C: C: O: (b) : O:: C ::C:: C : O:
(c) :Ö:: C:: C:: C:: Ö: (d) : O: C : C : C : O :

SECTION - II

More than One Options Correct Type

11. Compared to *meta* and *para* isomers, *o*-nitrophenol has
(a) lower solubility in water
(b) higher melting point and boiling point
(c) lower enthalpy of fusion
(d) all of these.

12. Which of the following pairs contain same number of electrons but their shapes are different?
(a) BF_3, BCl_3 (b) CH_4, NH_3
(c) NH_3, H_2O (d) $BeCl_2$, BeF_2

13. Hydrogen bonding is responsible for which of the following phenomena?
(a) Ice floats on water.
(b) Higher Lewis basicity of primary amines than tertiary amines in aqueous solutions.
(c) Formic acid is more acidic than acetic acid.
(d) Dimerisation of acetic acid in benzene.

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

The shapes of molecules can be predicted by VSEPR theory, hybridisation and dipole moment. Total number of hybrid orbitals (H) on the central atom of a molecule can be calculated by using the following relation :
H = 1/2[Total no. of valence electrons (P)–
3 × (no. of atoms surrounding the central atom, excluding hydrogen atoms)]
One can also calculate total no. of bond pairs (n) around central atom as
n = total number of atoms surrounding the central atom
Also, total no. of lone pairs (m) = $H - n$
Thus, VSEPR notation of a molecule can be written as AX_nE_m. Where, A denotes central atom of the molecule
X denotes bond pair on central atom of the molecule
E denotes lone pairs on central atom of the molecule
In a polar molecule, the net dipole moment of the molecule $\propto m$.

14. VSEPR notation of chlorine trifluoride molecule is
(a) AX_5 (b) AX_3 (c) AX_2E_3 (d) AX_3E_2

15. For the given molecules : CO_2(I), SO_2 (II), H_2O (III), the correct increasing order of their dipole moments is
(a) I < II < III (b) II < I < III
(c) III < II < I (d) III < I < II

Paragraph for Questions 16 and 17

According to the concept of resonance, whenever a single Lewis structure can't describe a molecule accurately, then a number of structures called resonating structures, with similar energy, same relative position of all nuclei and with same number of paired and unpaired electrons are drawn. The molecule as such has a single definite structure which is resonance hybrid of the resonating structures and can't as such be depicted by a single Lewis structure. As a result of resonance, the bond order may change in many molecules or ions and is given by formula,

$$\text{Bond order} = \frac{\text{Total number of bonds between two atoms in all the structures}}{\text{Total number of resonating structures}}$$

16. What is the bond order of benzene?
(a) 2 (b) 1.5 (c) 2.5 (d) 3.0

17. Bond order of N—O bonds in nitrate ion is
(a) 1.25 (b) 2.00 (c) 1.45 (d) 1.33

SECTION - IV

Matching List Type

18. Match the List I with List II and select the correct answer using the codes given below the lists :

	List I		List II
P.	XeF_4	1.	sp^3d, see-saw
Q.	SF_4	2.	sp^3d^2, square planar
R.	SF_6	3.	sp^3d^3, distorted octahedral
S.	XeF_6	4.	sp^3d^2, octahedral

	P	Q	R	S
(a)	4	1	2	3
(b)	2	1	4	3
(c)	2	1	3	4
(d)	1	2	4	3

19. Match the List I with List II and select the correct answer using the codes given below the lists :

	List I		List II
P.	H_3O^+	1.	Linear
Q.	$HC\equiv CH$	2.	Angular
R.	ClO_2^-	3.	Tetrahedral
S.	NH_4^+	4.	Trigonal bipyramidal
		5.	Pyramidal

	P	Q	R	S
(a)	1	2	3	4
(b)	5	1	2	3
(c)	1	2	5	3
(d)	3	2	4	1

SECTION - V

Assertion Reason Type

20. Assertion : The crystal structures get stabilized even though the sum of electron gain enthalpy and ionisation enthalpy is positive.

Reason : Energy is absorbed during the formation of crystal lattice.

21. Assertion : CO_2 molecules are linear.

Reason : The value of dipole moment of CO_2 is zero.

22. Assertion : Each H_2O molecule is linked to four H_2O molecules tetrahedrally.

Reason : Each H_2O molecule is linked to two H_2O molecules through covalent bonds and to two H_2O molecules through hydrogen bonds.

SECTION - VI

Integer Value Correct Type

23. The ratio of σ to π bonds in mesitylene is

24. Bond-order in NO^+ is

25. The number of species among the following which have fractional bond order is

Li_2, He_2^+, N_2^+, N_2^{2-}, O_2^+, O_2^{2-}, O_2^-, CO_3^{2-}, C_6H_6, O_3

HYDROGEN

SECTION - I

Only One Option Correct Type

1. Acidified $K_2Cr_2O_7$ on oxidation by H_2O_2 gives
(a) blue solution (b) CrO_5
(c) chromium peroxide (d) all of these.

2. In the method of bulk preparation of hydrogen by electrolytic method, the role of electrolyte is to
(a) decrease the boiling point of water
(b) increase the boiling point of water
(c) increase the ionisation of water
(d) increase the charge carrying particles in water.

3. Ozone is used for purifying water because
(a) it dissociates and release oxygen
(b) do not leave any foul smell like chlorine
(c) kills bacteria, cysts, fungi and acts as a biocide
(d) all of the above.

4. Metal that cannot displace hydrogen from dil. HCl is
(a) Al (b) Fe (c) Cu (d) Zn

5. Mass percentage of deuterium in heavy water is
(a) same as that of protium in water
(b) 11.1 (c) 20.0
(d) cannot be predicted.

6. Which of the following statements is not true?
(a) Ordinary water is electrolysed more rapidly than D_2O.
(b) Reaction between H_2 and Cl_2 is much faster than D_2 and Cl_2.
(c) D_2O freezes at lower temperature than H_2O.
(d) Bond dissociation energy for D_2 is greater than H_2.

7. Which among the following statements is incorrect?
(a) Ordinary hydrogen is an equilibrium mixture of ortho and para hydrogen.
(b) In ortho hydrogen spin of two nuclei is in same direction.
(c) Ortho and para forms do not resemble in their chemical properties.
(d) In para hydrogen spin of two nuclei is in opposite direction.

8. In which of the following reactions, H_2O_2 acts as a reducing agent
(a) $PbO_{2(s)} + H_2O_{2(aq)} \longrightarrow PbO_{(s)} + H_2O_{(l)} + O_{2(g)}$
(b) $Na_2SO_{3(aq)} + H_2O_{2(aq)} \longrightarrow Na_2SO_{4(aq)} + H_2O_{(l)}$
(c) $2KI_{(aq)} + H_2O_{2(aq)} \longrightarrow 2KOH_{(aq)} + I_{2(s)}$
(d) $KNO_{2(aq)} + H_2O_{2(aq)} \longrightarrow KNO_{3(aq)} + H_2O_{(l)}$

9. 100 mL of tap water containing $Ca(HCO_3)_2$ was titrated with N/50 HCl with methyl orange as an indicator. If 30 mL of HCl were required, the temporary hardness as parts of $CaCO_3$ per 10^6 parts of water is
(a) 150 (b) 300 (c) 450 (d) 600

10. The correct order of the O—O bond length in O_2 H_2O_2 and O_3 is
(a) $O_2 < O_3 < H_2O_2$ (b) $O_3 > H_2O_2 > O_2$
(c) $H_2O_2 > O_3 > O_2$ (d) $O_2 > H_2O_2 > O_3$

SECTION - II

More than One Options Correct Type

11. Which of the following statements are correct?
(a) Magnesium with dil. HNO_3 produces hydrogen.
(b) H_2O_2 bleaches by oxidation.
(c) H_2O_2 reduces $KMnO_4$ only in alkaline medium.
(d) The position of hydrogen is not fixed in periodic table.

12. Which of the following can be classified as hard water?
(a) Water containing some potash alum
(b) Water containing a few drops of HCl
(c) Water containing common salt
(d) Water containing calcium nitrate

13. Hydrogen is not produced by the reaction
(a) Na_2O_2 + dil. H_2SO_4 (b) $Mg + H_2O$
(c) $BaO_2 + HCl$ (d) $BaO_2 + H_3PO_4$

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

Concentration of H_2O_2 is expressed in terms of volume strength *e.g.*, 10 volume, 15 volume, 20 volume, H_2O_2 solution. It represents the volume of oxygen in mL obtained at NTP by the decomposition of 1 mL of H_2O_2 solution. For example, 20 volume of H_2O_2 solution means 1 mL of this solution on decomposition evolves 20 mL of O_2 at NTP. However, sometimes the concentration of H_2O_2 in a solution is expressed as percentage of H_2O_2 in solution (W/V).Thus 30% solution of H_2O_2 means 30 grams of H_2O_2 are present in 100 mL of water.

14. The percentage strength of H_2O_2 in a sample marked as 10 volume is
(a) 1.515% (b) 3.03% (c) 6.06% (d) 2.86%

15. When 25 mL of '30 volume' H_2O_2 is completely decomposed, the volume of oxygen gas liberated at STP is
(a) 30 mL (b) 900 mL (c) 250 mL (d) 750 mL

Paragraph for Questions 16 and 17

Research scholar '*P*' added zinc pieces into aqueous $FeCl_3$ solution and performed some experiments with resultant solution. Research scholar '*Q*' passed H_2 gas into aqueous $FeCl_3$ solution and performed some experiments with resultant solution.

16. Yellow coloured $FeCl_3$ solution changed to light green (appeared as colourless) in the experiment of
(a) *P* (b) *Q*
(c) Both (*P*) and (Q) (d) None of these.

17. Select the correct statement.
(a) Zn pieces liberate nascent hydrogen on reaction with acidic solution of $FeCl_3$.
(b) $FeCl_3$ solution is reduced to $FeCl_2$ in the experiments of *P* and *Q* both.
(c) Blue colour complex is formed in both the experiments on reaction with $K_4[Fe(CN)_6]$.
(d) All of the above.

SECTION - IV

Matching List Type

18. Match the List I with List II and select the correct answer using the codes given below the lists :

	List I (Hydride)		List II (Types of hydride)
P.	BeH_2	1.	Polynuclear
Q.	AsH_3	2.	Interstitial
R.	B_2H_6	3.	Covalent
S.	LaH_3	4.	Polymeric

	P	Q	R	S
(a)	4	3	1	2
(b)	4	1	3	2
(c)	1	2	4	3
(d)	3	2	4	1

19. Match the List I with List II and select the correct answer using the codes given below the lists :

	List I		List II
P.	Heavy water	1.	Bicarbonates of Mg and Ca in water
Q.	Temporary hard water	2.	No foreign ions in water
R.	Soft water	3.	D_2O
S.	Permanent hard water	4.	Sulphates and chlorides of Mg and Ca in water

	P	Q	R	S
(a)	1	2	3	4
(b)	4	3	1	1
(c)	3	2	1	4
(d)	3	1	2	4

SECTION - V

Assertion Reason Type

20. **Assertion :** H_2O_2 has higher boiling point than water.
Reason : It has stronger dipole-dipole interactions than that shown by water.

21. **Assertion :** In space crafts H_2 gas is used in fuel cells for generating electrical energy and for providing clean drinking water to the astronauts.
Reason : A fuel cell may have an alkaline or acidic electrolyte.

22. **Assertion :** Demineralised water does not contain any ions.
Reason : Permutit process for water softening gives demineralised water.

SECTION - VI

Integer Value Correct Type

23. A 3.2 cm^3 solution of H_2O_2 liberates 0.508 g of iodine from acidified KI solution. The strength of H_2O_2 solution in terms of volume strength (in mL) at STP is

24. Two moles of MnO_4^- reduce x mole(s) of H_2O_2 in basic medium. The value of x is

25. The total number of metals from the given list which will give H_2 on reaction with NaOH is
Zn, Mg, Al, Be

SOLUTIONS

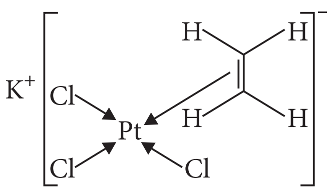
CHEMICAL BONDING AND MOLECULAR STRUCTURE

1. **(d) :** For greater ionic character of the bond, the cation should have low polarising power and the anion should have small polarisability.

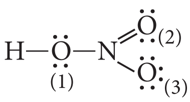
2. **(b) :** $37 = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 5s^1$
Thus, the element belongs to group 1 and has valency + 1.
$53 = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 5s^2, 5p^5$
Since, there are 7 electrons in the valence shell, thus this element belongs to group 17 and requires one electron to complete its octet *i.e.*, has valency–1.
Hence, element with atomic number 37 transfers its electron to the element having atomic number 53 and results in the formation of an ionic bond.

3. **(d)**

4. **(d) :** Zeise's salt is



It has ionic, covalent (in ethylene molecule) and coordinate bonds.

5. **(b) :** 

Formal charge on an atom in a Lewis structure
= [Total number of valence electrons in free atom]
– [Total number of non-bonding (lone pairs) electrons]
$-\frac{1}{2}$ [Total number of bonding or shared electrons]

Formal charge on $H = 1 - 0 - \frac{1}{2} \times 2 = 0$

Formal charge on $N = 5 - 0 - \frac{1}{2} \times 8 = 1$

Formal charge on $O(1) = 6 - 4 - \frac{1}{2} \times 4 = 0$

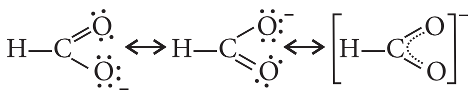
Formal charge on $O(2) = 6 - 4 - \frac{1}{2} \times 4 = 0$

Formal charge on $O(3) = 6 - 6 - \frac{1}{2} \times 2 = -1$

6. **(c) :** Since, water is polar in nature and like dissolves like, the coating must be nonpolar to polar manner.

7. **(b) :** According to Hannay and Smith equation,
% ionic character = $16(\chi_A - \chi_B) + 3.5\,(\chi_A - \chi_B)^2$
where χ_A and χ_B are electronegativities of the atom A and B respectively.
$\therefore$ % ionic character = $16(2) + 3.5\,(2)^2$
$= 32 + 14 = 46$

8. **(b) :** As the number of lone pairs of electrons increases, bond angle decreases. Thus, the order of bond angle is
$NH_4^+ > NH_3 > NH_2^-$
(no *lp*) (1 *lp*) (2 *lp*)

9. **(c) :** 

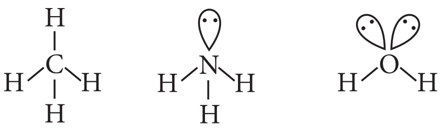
Resonance hybrid

Due to resonance, C—O bond lengths are same.

10. (c) : In structure (c), all the atoms have complete octet. Thus, it is the correct representation of carbon suboxide.

11. (a,c) : In contrast to *meta* and *para*-isomers, *o*-nitrophenol has intramolecular H-bonding which prevents association resulting in lower melting point and boiling point, decrease in enthalpy of fusion and decrease of solubility in water.

12. (b,c) : The central atom in each of three molecules CH_4, NH_3 and H_2O undergoes sp^3 hybridisation. In CH_4 no lone pair is present. In NH_3 one lone pair is present while in water two lone pairs are present.



Tetrahedral (109°.28′) | Pyramidal structure (106.5°) | V-structure (104.5°)

13. (a,b,d)

14. (d): Number of hybrid orbitals, H in $ClF_3 = \frac{1}{2}$ (Valence electrons of Cl + 3 × valence electrons of F) – 3 × 3 F– atoms) $= \frac{1}{2}(7+3\times7)-9=14-9=5$

Number of bond pairs (n) = 3

Total number of lone pairs (m) = $H - n = 5 - 3 = 2$

Hence, VSEPR notation of ClF_3 is AX_3E_2.

15. (a): $CO_2: H = \frac{1}{2}(4+2\times6)-3\times2=2;$

$n = 2; m = H - n = 2 - 2 = 0$

$SO_2;\ H = \frac{1}{2}(6+2\times6)-3\times2=3;$

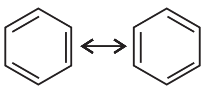
$n = 2; m = 3 - 2 = 1$

$H_2O: H = \frac{1}{2}(2\times1+6)-3\times0=4;$

$n = 2; m = 4 - 2 = 2$

Hence, correct order of dipole moments :

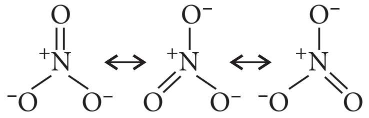
$CO_2 < SO_2 < H_2O$

16. (b): 

$$\text{Bond order} = \frac{\text{Total number of bonds between two C-atoms in all structures}}{\text{Total number of resonating structure}}$$

$$= \frac{2+1}{2} = 1.5$$

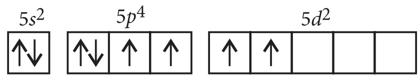
17. (d): Nitrate ion has the following three resonating structures :



Three O-atoms are attached to the N-atom by four bonds, therefore, bond order of N—O bond is $\frac{4}{3} = 1.33$.

18. (b): P-(2); Q-(1); R(4); S-(3)

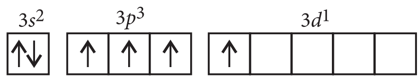
(P) XeF_4, Xe(54) :



(excited state)

sp^3d^2 hybridisation, two lone pairs of electrons occupy two vertices of octahedron while 4 vertices are occupied by 4 F-atoms hence, square planar geometry.

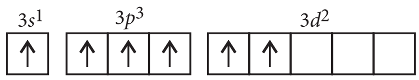
(Q) SF_4, S(16) :



(excited state)

sp^3d hybridisation – square pyramidal

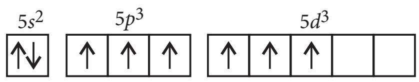
(R) SF_6, S(16) :



(excited state)

sp^3d^2 hybridisation – octahedral geometry

(S) XeF_6, Xe(54) :



(excited state)

sp^3d^3 hybridisation-distorted octahedral geometry The hybrid orbitals will be directed towards 7 vertices of pentagonal bypyramid. Since one of the vertex is occupied by a lone pair, actual geometry is distorted octahedral.

19. (b): (a) $H_3O^+ = 3\ bp + 1lp \Rightarrow$ pyramidal

(b) $HC \equiv CH \Rightarrow$ linear as sp hybridised

(c) $ClO_2^- \Rightarrow 2\ bp + 2\ lp \Rightarrow$ angular

(d) $NH_4^+ \Rightarrow 4bp + 0\ lp \Rightarrow$ tetrahedral

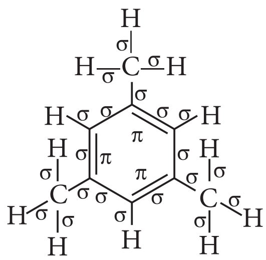
20. (c): Energy is released in the formation of the crystal lattice. It is a qualitative measure of the stability of an ionic compound.

21. (a) : The value of dipole moments provide valuable information about the structure of molecules.

$$\overset{\leftarrow\!\!+}{O{=}}C\overset{+\!\!\rightarrow}{=O}$$
$$\mu = 0$$

22. (c) : Each H_2O molecule is linked to four other H_2O molecules through hydrogen bonds.

23. (7) : The structure of mesitylene is



Total number of σ-bonds = 21

Total number of π-bonds = 3

$\therefore$ Ratio of σ to π bonds $= \dfrac{21}{3} = 7$

24. (3) : $NO^+ = KK[\sigma(2s)]^2[\sigma^*(2s)]^2[\sigma(2p_z)]^2[\pi(2p_x)]^2[\pi(2p_y)]^2$

Bond order $= \dfrac{1}{2}(8-2) = 3$

25. (7) : $Li_2 = 1,\ He_2^+ = \dfrac{1}{2},\ N_2^+ = 2\dfrac{1}{2},\ N_2^{2-} = 2,$

$O_2^+ = 2.5, O_2^{2-} = 1.0, O_2^- = 1.5, CO_3^{2-} = 1.33,$

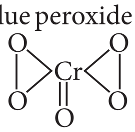
$C_6H_6 = 1.5,\ O_3 = 1.5$

HYDROGEN

1. (b) : $K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + H_2Cr_2O_7$

$H_2Cr_2O_7 + 4H_2O_2 \longrightarrow \underset{\text{Blue}}{2CrO_5} + 5H_2O$

CrO_5 is blue peroxide of chromium and has butterfly structure



2. (d) : Electrolysis of acidified water using platinum electrodes gives hydrogen.

$$2H_2O_{(l)} \xrightarrow[\text{Traces of acid/base}]{\text{Electrolysis}} 2H_{2(g)} + O_{2(g)}$$

The role of an electrolyte is to make water conducting by increasing the number of charge carrying particles, *i.e.*, ions.

3. (d) : Ozone is used to purify water $\rightarrow$ Ozone kills bacteria, cysts, fungi, mold, parasites, viruses, contaminates etc. It is one of the effective ways of eliminating microorganisms in water. Ozone also oxidises toxins and odours. O_3 is most effective oxidant (secondary to F_2). It inactivates and oxidises organic matter, contaminates, pesticides, viruses and bacteria faster than chlorine. O_3 does not form TMH which have unpleasant odour and are also carcinogenic. O_3 is very good biocide. Ozone also absorbs UV radiation.

4. (c) : Cu is below hydrogen in the electrochemical series hence, cannot evolve H_2 with acids.

5. (c) : The formula of heavy water is D_2O, *i.e.*, molecular mass = 20

$\therefore$ % of deuterium $= \dfrac{4}{20} \times 100 = 20$

6. (c) : D_2O has higher freezing point (3.8°C) than H_2O(0°C).

7. (c) : Ortho and para forms of hydrogen resemble in their chemical properties.

8. (a)

9. (b) : 30 mL N/50 HCl $\equiv$ 30 mL N/50 $Ca(HCO_3)_2 \equiv$ 30 mL N/50 $CaCO_3 \equiv$ 100 mL tap water

Mass of $CaCO_3$ in 100 mL tap water $= \dfrac{E \times N \times V}{1000}$

$= \dfrac{50 \times 30}{50 \times 1000} = 0.03$ g

$\Rightarrow$ hardness = 300 ppm

10. (c) : In H_2O_2, there is a single bond between O—O, in O_3 there is resonance between a single and a double bond and in O_2 there is double bond. Therefore, the O—O bond length decreases in the order :

$$\underset{147.5\text{ pm}}{H_2O_2} > \underset{128\text{ pm}}{O_3} > \underset{121\text{ pm}}{O_2}$$

11. (a,b,d) : H_2O_2 reduces $KMnO_4$ in both alkaline and acidic medium.

12. (a,b,d) : Water containing any cation other than NH_4^+ and alkali metal is hard water.

MPP-3 CLASS XI ANSWER KEY

1.	(d)	**2.**	(b)	**3.**	(d)	**4.**	(a)	**5.**	(d)
6.	(d)	**7.**	(c)	**8.**	(a)	**9.**	(a)	**10.**	(b)
11.	(c)	**12.**	(c)	**13.**	(c)	**14.**	(a)	**15.**	(d)
16.	(a)	**17.**	(a)	**18.**	(c)	**19.**	(c)	**20.**	(a,d)
21.	(a,d)	**22.**	(b,c)	**23.**	(a,b,c)	**24.**	(7)	**25.**	(4)
26.	(8)	**27.**	(c)	**28.**	(a)	**29.**	(b)	**30.**	(a)

13. (a,c,d) : $Mg + H_2O \xrightarrow{\Delta} Mg(OH)_2 + H_2$, other reactions produce H_2O_2.

14. (b): By definition, we know that 1 mL of 10 volume H_2O_2 gives 10 mL of O_2 at NTP.

From the equation,

$$\underset{2(2+32)=68\text{ g}}{2H_2O_2} \longrightarrow 2H_2O + \underset{22400\text{ mL at NTP}}{O_2}$$

22400 mL of O_2 at NTP are obtained from 68 g of H_2O_2

10 mL of O_2 at NTP are obtained from

$$= \frac{68}{22400} \times 10\text{ g of } H_2O_2 = \frac{68}{2240}\text{ g of } H_2O_2$$

Now, since 1 mL of the given H_2O_2 solution contains

$$= \frac{68}{2240}\text{ g of } H_2O_2$$

100 mL of the given H_2O_2 solution contain

$$= \frac{68}{2240} \times 100 = 3.03\%$$

15. (d): 1 mL of '30 volume' H_2O_2 gives 30 mL of O_2 at STP.

$\therefore$ 25 mL of '30 volume' H_2O_2 gives 30 × 25 mL of O_2 at STP = 750 mL of O_2 at STP.

16. (a): In the experiment of scholar *P*, the colour gets changed because nascent hydrogen is obtained on adding zinc which is more reactive. The nascent hydrogen reduces Fe^{3+} to Fe^{2+}.

Molecular H_2 does not react with $FeCl_3$.

17. (a): Zn generates nascent H.

$FeCl_3 + [H] \longrightarrow FeCl_2 + HCl$

18. (a): P-4; Q-3; R-1; S-2

19. (d): P-3; Q-1; R-2; S-4

20. (a): Hydrogen bonding is a special case of dipole-dipole interaction and hydrogen peroxide is more hydrogen bonded than water.

21. (b)

22. (c): Water softened by Permutit process is not demineralised water since it still contains sodium salts.

23. (7): H_2SO_4 + KI shows the following change :

$2I^- \longrightarrow I_2 + 2e^-$

$O_2^{2-} + 2e^- \longrightarrow 2O^{2-}$

or $H_2O_2 + H_2SO_4 + 2KI \longrightarrow K_2SO_4 + I_2 + 2H_2O$

Now meq. of H_2O_2 = meq. of I_2

$$N \times 3.2 = \frac{0.508\text{ g}}{254/2} \times 1000$$

$$\therefore\ N_{H_2O_2} = \frac{4\text{ g}}{3.2} = 1.25\text{ eq/L}$$

$$\therefore\ w_{H_2O_2} = \frac{1.25 \times 34}{2} = 21.25\text{ g/L} = 0.02125\text{ g/mL}$$

As 68 g H_2O_2 gives O_2 at NTP = 22400 mL

$\therefore$ 0.02125 g or 1 mL H_2O_2 gives O_2

$$= \frac{22400 \times 0.02125}{68} = 7\text{ mL}$$

$\therefore$ Volume strength of H_2O_2 = 7 mL

24. (3): $2MnO_4^- + 3H_2O_2 \longrightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^-$

25. (3): $Zn + 2NaOH \xrightarrow{\text{Heat}} Na_2ZnO_2 + H_2$

$2Al + 2NaOH + 2H_2O \xrightarrow{\text{Heat}} 2NaAlO_2 + 3H_2$

$Be + 2NaOH \longrightarrow Na_2BeO_2 + H_2$

SOLUTIONS OF AUGUST 2016 CROSSWORD

				1 D		2 S	T	3 A	R	C	H			4 E	T	H	5 E	R	A	T	E	S	
				R				L									N						
6 P	H	O	N	O	N			K			7 A	N	T	A	C	I	D	S					
				S		8 E		A									E						
				9 S	E	L	E	N	I	U	M			10 T	H	E	R	M	I	T	11 E		
	12 W					E		E									G				I		
	H					C		S				13 P	I	N	A	C	O	L	S		G		
	I					T			14 M								N				H		
	15 T	U	R	G	O	R			16 I	N	S	T	A	B	17 I	L	I	T	Y		T		
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			18 A			19 N	I	T	R	O	S	A	T	I	O	N							
	20 I		N			S			O						M								
	N		T		21 H				C				22 K		O								
	V		I		I			23 I	O	D	I	M	E	T	R	I	C			24 H			
	E		C		S				S				T		P			25 Y		A			26 F
	R		H		T				M		27 G	R	A	P	H	I	T	E		L			I
	28 S	O	L	V	O	L	Y	S	I	S			L		S			L		O			B
	I		O		N				C									29 L	I	N	E	A	R
	O		R		E													O		S			E
	N				30 S	P	I	N	E	L								W					S

Winners of July 2016 Crossword

- Ashwin Shenoy, Mangaluru
- Devjit Acharjee, Kolkata

Solution Senders of Chemistry Musing

Set - 37

- Sakshi Sehgal, Bengaluru
- Joyshree Das, Kolkata

Set - 36

- Sanjay Joshi, Ranchi
- Amit Kumar, Mumbai

CLASS XI Series 3

ACE YOUR WAY CBSE

States of Matter Thermodynamics

Time Allowed : 3 hours
Maximum Marks : 70

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
(iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
(v) Q. no. 23 is a value based question and carries 4 marks.
(vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

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1. Boyle's law states that at constant temperature, if pressure is increased on a gas, volume decreases and vice-versa, but when we fill air in a balloon, volume as well as pressure increase. Why?

2. The magnitude of surface tension of liquid depends on the attractive forces between the molecules. Arrange the following, in increasing order of surface tension : Water, alcohol (C_2H_5OH) and hexane [$CH_3(CH_2)_4CH_3$)].

3. Heat capacity (C_p) is an extensive property but specific heat (c) is an intensive property. What will be the relation between C_p and c for 1 mol of water?

4. In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy of the process?

5. Write the conditions in terms of ΔH and ΔS when a reaction would be always spontaneous.

6. Although heat is a path function but heat absorbed by the system under certain specific conditions is independent of path. What are those conditions? Explain.

7. An open vessel contains 200 mg of air at 17°C. What weight percent of air would be expelled if the vessel is heated to 117°C ?

8. The standard heat of formation of $CH_{4(g)}$, $CO_{2(g)}$ and $H_2O_{(g)}$ are – 76.2, – 394.8 and – 241.6 kJ mol^{-1} respectively. Calculate the amount of heat evolved by burning 1 m^3 of methane measured at NTP.

9. The density of steam at 100°C and 10^5 Pa pressure is 0.6 kg m^{-3}. Calculate the compressibility factor of steam.

OR

A neon dioxygen mixture contains 70.6 g O_2 and 167.5 g Ne. If pressure of the mixture of gases in the cylinder is 25 bar, what is the partial pressure of O_2 and Ne in the mixture?

10. An iron cylinder contains helium at a pressure of 250 kPa at 300 K. The cylinder can withstand a pressure of 1×10^6 Pa. The room in which cylinder is placed catches fire. Predict whether the cylinder will blow up before it melts or not. (M.Pt. of the cylinder = 1800 K).

11. Calculate the work done when 11.2 g of iron dissolves in hydrochloric acid in

(i) a closed vessel

(ii) an open beaker at 25°C

(Atomic mass of Fe = 56 u)

12. (i) Calculate the total pressure in a mixture of 8 g of dioxygen and 4 g of hydrogen confined in a vessel of 1 dm^3 at 27°C ($R = 0.083$ bar dm^3 K^{-1} mol^{-1})

(ii) Critical temperature for carbon dioxide and methane are 31.1°C and –81.9°C respectively. Which of these has stronger intermolecular forces and why?

13. The pressure exerted by 12 g of an ideal gas at temperature t°C in a vessel of volume V litre is 1 atm. When the temperature is increased by 10°C at the same volume, the pressure increases by 10%. Calculate the temperature t and volume V. (Molecular weight of the gas is 120)

14. The enthalpy of vaporisation of liquid diethyl ether $(C_2H_5)_2O$ is 26.0 kJ mol^{-1} at its boiling point (35.0°C). Calculate $\Delta S°$ for the conversion of

(i) liquid to vapour and

(ii) vapour to liquid at 35°C.

15. 1 g of graphite is burnt in a bomb calorimeter in excess of oxygen at 298 K and 1 atmospheric pressure according to the equation

$$C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}$$

During the reaction, temperature rises from 298 K to 299 K. If the heat capacity of the bomb calorimeter is 20.7 kJ/K, what is the enthalpy change for the above reaction at 298 K and 1 atm?

OR

At 25°C the standard enthalpies of combustion of hydrogen, cyclohexene (C_6H_{10}), and cyclohexane (C_6H_{12}) are – 241, – 3800, and – 3920 kJ mol^{-1}, respectively. Calculate the heat of hydrogenation of cyclohexene.

16. For the reaction, $2A_{(g)} + B_{(g)} \rightarrow 2D_{(g)}$; $\Delta U° = -\ 10.5$ kJ and $\Delta S° = -\ 44.1$ JK^{-1}.

Calculate $\Delta G°$ for the reaction and predict whether the reaction may occur spontaneously or not.
($R = 8.314 \times 10^{-3}$ kJ K^{-1} mol^{-1}, $T = 298$ K)

17. Explain the following :

(i) The boiling point of a liquid rises on increasing pressure.

(ii) Drops of liquids assume spherical shape.

(iii) The level of mercury in a capillary tube is lower than the level outside when a capillary tube is inserted in the mercury.

18. Explain the term Laminar Flow. Is the velocity of molecules same in all the layers in laminar flow? Explain your answer.

19. A 2.0 L container at 25°C contains 1.25 moles of oxygen and 3.2 moles of carbon.

(i) What is the initial pressure in the flask?

(ii) If the carbon and oxygen react as completely as possible to form CO, what will be the final pressure in the container?

20. At sea level, the composition of dry air is approximately $N_2 = 75.5\%$, $O_2 = 23.2\%$, and Ar = 1.3% by mass. If the total pressure at sea level is 1 bar, what is the partial pressure of each component?

21. A gas cylinder contains 370 g oxygen at 30.0 atm pressure and 25°C. What mass of oxygen will escape if the cylinder is first heated to 75°C and then the valve is held open until gas pressure becomes 1.0 atm, the temperature being maintained at 75°C?

22. The van der Walls' constant 'b' for oxygen is 0.0318 L mol^{-1}. Calculate the diameter of the oxygen molecule.

23. A school has a four storeyed building. Some students have their classes on the 3rd and 4th floor of the building. Many students go by the staircase whereas some go by elevator. It is observed that students going by steps feel more fresh throughout the day as compared to those who go by the elevator.

(i) What values are expressed in the above paragraph ?

(ii) Comment on the thermodynamic nature of the work done by two students, one who took the staircase and the other went by elevator when they have reached the same floor?

(iii) Student going by staircase should feel tired instead, why does he/she feel fresh throughout the day? Which law applies here and how?

24. (i) A cylinder of 20.0 L capacity contains 160 g of oxygen gas at 25°C. What mass of oxygen must be released to reduce the pressure of the cylinder to 1.2 atm?

(ii) Compressibility factor, Z, of a gas is given as $Z = \dfrac{PV}{nRT}$

(a) What is the value of Z for an ideal gas?

(b) For real gas what will be the effect on value of Z above Boyle's temperature?

OR

(i) Pay load is defined as the difference between the mass of the displaced air and the mass of the balloon. Calculate the pay load when a balloon of radius 10 m, mass 100 kg is filled with helium at 1.66 bar at 27°C (Density of air = 1.2 kg m^{-3} and R = 0.0833 bar dm^3 K^{-1} mol^{-1})

(ii) Calculate the volume occupied by 8.8 g of CO at 31.1°C and 1 bar pressure
(R = 0.083 bar L K^{-1} mol^{-1})

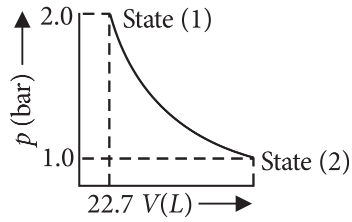
25. (i) Work done in the expansion of an ideal gas from 4 dm^3 to 6 dm^3 against a constant external pressure of 2.5 atm was used to heat up 1 mole of water at 20°C. What will be the final temperature of water. Given that the specific heat of water = 4.184 J g^{-1} K^{-1}.

(ii) At 0°C, ice and water are in equilibrium and ΔH = 6.00 kJ mol^{-1} for the process $H_2O_{(s)} \rightarrow H_2O_{(l)}$. What will be ΔS and ΔG for the conversion of ice to liquid water?

OR

(i) Calculate the enthalpy change on freezing of 1.0 mole of water at 10.0°C to ice at – 10.0°C.
$\Delta_{fus}H$ = 6.03 kJ mol^{-1} at 0°C.
$C_p\,[H_2O_{(l)}]$ = 75.3 J K^{-1} mol^{-1},
$C_p\,[H_2O_{(s)}]$ = 26.8 J K^{-1} mol^{-1}

(ii) 1.0 mole of a monoatomic ideal gas is expanded from state (1) to state (2) as shown in figure. Calculate the work done for the expansion of gas from state (1) to state (2) at 298 K.



26. Compute the heat of formation of liquid methyl alcohol (in kJ mol^{-1}) using the following data. The heat of vaporisation of liquid methyl alcohol is 38 kJ mol^{-1}. The heat of formation of gaseous atoms from the elements in their standard states. H = 218 kJ mol^{-1}, C = 715 kJ mol^{-1}, O = 249 kJ mol^{-1}.
Average bond energies :
C—H = 415 kJ mol^{-1}
C—O = 356 kJ mol^{-1}
O—H = 463 kJ mol^{-1}

OR

(i) For the reaction, $Ag_2O_{(g)} \rightarrow 2Ag_{(s)} + \frac{1}{2}O_{2(g)}$;
ΔH = 30.56 kJ mol^{-1} and ΔS = 6.66 J K^{-1} mol^{-1} at 1 atm. Calculate the temperature at which ΔG is equal to zero. Also predict the direction of the reaction at (i) this temperature and (ii) below this temperature.

(ii) Calculate the work-done when 1 mole of an ideal gas expands reversibly and isothermally from a volume of 1 litre to a volume of 10 litres at 27°C and normal pressure.

SOLUTIONS

1. The law is applicable only for a definite mass of the gas. As air is filled into the balloon, more and more air is introduced into the balloon and the mass of air inside is increased hence, the law is not applicable.

2. In hexane, there are only London dispersion forces between the molecules. These forces are very weak. H-bonding is stronger in H_2O in comparison to C_2H_5OH. Hence, the increasing order of surface tension is
Hexane < Alcohol < Water.

3. For water, molar heat capacity (C_p) = 18 × specific heat
∴ $C_p = 18 \times c$

4. q = + 701 J, w = – 394 J, ΔU = ?
By first law of thermodynamics $\Delta U = q + w$
= + 701 J + (–394 J) = + 307 J
i.e., internal energy of the system increases by 307 J.

5. The reaction would be always spontaneous when both energy factor and randomness factor favour it, *i.e.*, $\Delta H = -$ ve and $\Delta S = +$ ve.

6. The two conditions under which heat becomes independent of path are :

   (i) When volume remains constant :
   By first law of thermodynamics,
   $\Delta U = q + w$ or $q = \Delta U - w$. $\because w = -p\Delta V$. Hence, $q = \Delta U + p\Delta V$.
   As volume is constant, $\Delta V = 0$.
   $\therefore \quad q_V = \Delta U$
   As ΔU is a state function so, q_V is a state function.

   (ii) When pressure remains constant :
   $q_p = \Delta U + p\Delta V$.
   $\because \Delta U + p\Delta V = \Delta H$
   $\because q_p = \Delta H$
   As ΔH is a state function therefore, q_p is a state function.

7. Suppose volume of 200 mg of air at 17°C = V mL
As pressure remains constant (being an open vessel), applying Charles' law,
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}, \text{ i.e., } \frac{V}{290} = \frac{V_2}{390} \text{ or } V_2 = 1.34\,V$$
$\therefore$ Volume of air expelled = 1.34 V – V = 0.34 V
Mass of 1.34 V air at 117°C = 200 mg
Mass of 0.34 V air at 117°C = $\frac{200}{1.34} \times 0.34$ mg
$\therefore$ Mass % of air expelled
$$\frac{200 \times 0.34}{1.34} \times \frac{1}{200} \times 100 = 25.37\%$$

8. The burning of methane may be expressed as
$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$
$\Delta_f H° = [\Delta_f H° (CO_2) + 2\Delta_f H° (H_2O)] - [\Delta_f H° (CH_4) + 2\Delta_f H° (O_2)]$
$= [-394.8 + 2 \times (-241.6)] - [-76.2 + 2 \times (0)]$
$= -801.8$ kJ
1 mole or 22.4 L of CH_4 evolve heat = 801.8 kJ
1 m^3 or 1000 L of CH_4 evolve heat $= \frac{801.8 \times 1000}{22.4}$
$= 35794.6$ kJ

9. $Z = \frac{PV}{nRT}$ and $d = \frac{PM}{RT}$
Using above equations, we get
$$Z = \frac{PV}{(w/M)RT} = \frac{MPV}{wRT} = \frac{MP}{dRT}$$
Therefore, on substituting all the values
$$Z = \frac{(18 \times 10^{-3}\ \text{kg mol}^{-1}) \times (10^5\ \text{N m}^{-2})}{(0.6\ \text{kg m}^{-3}) \times (8.31\ \text{N m K}^{-1}\ \text{mol}^{-1}) \times (373.15\ \text{K})}$$
$= 0.967$

OR

Moles of O_2 $(n_{O_2}) = \frac{70.6\text{ g}}{32\text{ g mol}^{-1}} = 2.21$ mol
Mole of Ne $(n_{Ne}) = \frac{167.5\text{ g}}{20\text{ g mol}^{-1}} = 8.375$ mol
Mole fraction of $O_2 (x_{O_2}) = \frac{2.21}{2.21 + 8.375} = 0.21$
Mole fraction of Ne $(x_{Ne}) = 1 - 0.21 = 0.79$
$p_{O_2} = x_{O_2} \times P_{total} = 0.21 \times (25\text{ bar}) = 5.25$ bar
$p_{Ne} = x_{Ne} \times P_{total} = 0.79 \times (25\text{ bar}) = 19.75$ bar

10. $P_1 = 250$ kPa, $T_1 = 300$ K
$P_2 = ?$ $T_2 = 1800$ K
Applying pressure – temperature law, $\frac{P_1}{T_1} = \frac{P_2}{T_2}$
$$\frac{250}{300} = \frac{P_2}{1800} \quad \text{or} \quad P_2 = 1500\ \text{kPa}$$
As the cylinder can withstand a pressure of 10^6 Pa $= 10^3$ kPa = 1000 kPa, hence, it will blow up.

11. Iron reacts with HCl acid to produce H_2 gas as
$Fe_{(s)} + 2HCl_{(aq)} \rightarrow FeCl_{2(aq)} + H_{2(g)}$
Thus, 1 mole of Fe, *i.e.*,56 g Fe produces H_2 gas = 1 mol.
$\therefore$ 11.2 g Fe will produce H_2 gas $= \frac{1}{56} \times 11.2 = 0.2$ mol

   (i) If the reaction is carried out in a closed vessel, $\Delta V = 0$
   $\therefore \quad w = -p_{ext}\,\Delta V = 0$

   (ii) If the reaction is carried out in an open beaker (external pressure being 1 atm)
   Initial volume = 0 (because no gas is present)
   Final volume occupied by 0.2 mole of H_2 at 25°C and 1 atm pressure can be calculated as follows :
   $PV = nRT$
   $\therefore \quad V = \frac{nRT}{P}$
   $$= \frac{0.2\text{ mol} \times 0.0821\text{ L atm K}^{-1}\text{ mol}^{-1} \times 298\text{ K}}{1\text{ atm}}$$
   $= 4.89$ L
   $\therefore \quad \Delta V = V_{final} - V_{initial} = 4.89$ L
   $w = -p_{ext}\,\Delta V = -1\text{ atm} \times 4.89$ L
   $= -4.89$ L atm $= -4.89 \times 101.3$ J
   $= -495.4$ J

12. (i) Moles of O_2, $n_{O_2} = \frac{\text{mass}}{\text{mol. wt.}} = \frac{8}{32} = 0.25$ mol

Moles of H_2, $n_{H_2} = \frac{4}{2} = 2.0$ mol

Total number of moles = 0.25 + 2.0 = 2.25 mol

Pressure, $P = \frac{nRT}{V}$

$$= \frac{2.25 \text{ mol} \times 0.083 \text{ bar dm}^3\text{K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{1 \text{ dm}^3}$$

$P = 56.025$ bar

(ii) $[T_c(CO_2) = -31.1°C] > [T_c(CH_4) = -81.9°C]$

Thus, intermolecular forces of attractions are greater in CO_2. This is due to higher molecular mass of CO_2]

13. $PV = nRT$

$$PV = nRT = \frac{w}{M}RT$$

$$1 \times V = \frac{12}{120} \times R \times (273 + t) \quad ....(i)$$

$$1.1 \times V = \frac{12}{120} \times R \times (273 + t + 10) \quad ...(ii)$$

Dividing eq. (ii) by eq. (i), we get

$$1.1 = \frac{(273 + t + 10)}{(273 + t)}$$

or $t = -173°C$

Putting this value in eq. (i), we get

$$1 \times V = \frac{12}{120} \times 0.0821 \times (273 - 173)$$

or $V = 0.821$ L

14. (i) For vaporisation of diethyl ether,

$$\therefore \quad \Delta_{vap}S° = \frac{\Delta_{vap}H°}{T}$$

$\Delta_{vap}H° = 26.0$ kJ mol^{-1}, $T = 273 + 35 = 308$ K

$$\Delta_{vap}S° = \frac{26.0 \times 10^3 \text{ J mol}^{-1}}{308 \text{ K}} = 84.4 \text{ JK}^{-1} \text{ mol}^{-1}$$

(ii) The conversion of vapour into liquid is condensation. The enthalpy of condensation is negative of enthalpy of vaporisation.

$\Delta_{vap}H° = -\Delta_{cond}H°$

$\therefore$ For condensation of diethyl ether (*i.e.*, conversion of vapour to liquid)

$$\Delta_{cond}S° = \frac{\Delta_{cond}H°}{T} = \frac{-26.0 \times 10^3 \text{ mol}^{-1}}{308}$$

$$= -84.4 \text{ JK}^{-1} \text{ mol}^{-1}$$

15. In bomb calorimeter, volume remains constant thus, the heat involved is internal energy *i.e.*, ΔU.

$\Delta U = q_v = C_v \Delta T$

Since, heat is lost by the system,

$\therefore \quad q_v = -C_v \Delta T = -20.7$ kJ/K $\times$ (299 – 298) K $= -20.7$ kJ

(Here, negative sign indicates the exothermic nature of the reaction.)

Thus, ΔU for the combustion of 1 g of graphite $= -20.7$ kJ

and ΔU for combustion of 1 mole (12.0 g) of graphite

$$= \frac{12.0 \text{ g mol}^{-1} \times (-20.7 \text{ kJ})}{1 \text{ g}} = -2.48 \times 10^2 \text{ kJ mol}^{-1}$$

Since, $\Delta n_g = 0$, $\Delta H = \Delta U = -2.48 \times 10^2$ kJ mol^{-1}

OR

The required reaction is

$$\underset{\text{Cyclohexene}}{C_6H_{10}} + H_2 \rightarrow \underset{\text{Cyclohexane}}{C_6H_{12}}, \ \Delta H_1 = ? \quad ...(i)$$

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O, \ \Delta H_2 = -241 \text{ kJ mol}^{-1} \quad ...(ii)$$

$$C_6H_{10} + \frac{17}{2}O_2 \longrightarrow 6CO_2 + 5H_2O, \ \Delta H_3 = -3800 \text{ kJ mol}^{-1} \quad ...(iii)$$

$$C_6H_{12} + 9O_2 \longrightarrow 6CO_2 + 6H_2O, \ \Delta H_4 = 3920 \text{ kJ mol}^{-1} \quad ...(iv)$$

The required equation (i) can be obtained by adding equations (ii) and (iii) and subtracting equation (iv) from the sum of equations (ii) and (iii).

$\Delta H_1 = (\Delta H_2 + \Delta H_3) - \Delta H_4$

$= [-241 + (-3800)] - (-3920)$

$= (-241 - 3800) - (-3920)$

$= -4041 + 3920 = -121$ kJ mol^{-1}

16. $2A_{(g)} + B_{(g)} \rightarrow 2D_{(g)}$;

$\Delta n_g = n_p - n_r = 2 - 3 = -1$

$\Delta H° = \Delta U° + \Delta n_g RT$

$\Delta H° = -10.5$ kJ $+ (-1 \text{ mol} \times 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \times 298 \text{ K})$

$= -12.977$ kJ

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta G° = -12.98 \text{ kJ} - (298 \text{ K} \times -44.1 \times 10^{-3} \text{ kJ K}^{-1})$

$= +0.16$ kJ

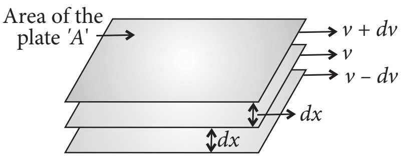
The reaction will not occur spontaneously because $\Delta G°$ is positive.

17. (i) A liquid boils when its vapour pressure becomes equal to the atmospheric pressure. An increase in pressure on liquid, causes a rise in the boiling temperature of the liquid.

(ii) Liquids have a property, called surface tension, due to which liquids tend to contract to decrease the surface area. For a given volume of the liquid, since a sphere has the least surface area, hence the liquids tend to form spherical drops.

(iii) The cohesive forces in mercury are much stronger than the force of adhesion between glass and mercury. Therefore, mercury-glass contact angle is greater than 90°. As a result, the vertical component of the surface tension forces acts vertically downward, thereby lowering the level of mercury column in the capillary tube.

18. When a liquid flows over a fixed surface, the layer of molecules in the immediate contact of surface is stationary. The velocity of the upper layer increases as the distance of layer from the fixed layer increases. This type of flow in which there is a regular gradation of velocity in passing from one layer to the next is called laminar flow. In laminar flow, the velocity of molecules is not same in all the layers because every layer offers some resistance or friction to the layer immediately below it.



Gradation of velocity in the laminar flow

19. (i) The container contains 1.25 moles of oxygen and 3.2 moles of carbon. Initial pressure in the flask will be only due to oxygen as carbon being solid will not exert any pressure.

n = 1.25 mol, V = 2.0 L, T = 273 + 25 = 298 K

$$\therefore \quad P = \frac{nRT}{V}$$

$$= \frac{(1.25\text{ mol})\times(0.0821\text{ L atm mol}^{-1}\text{ K}^{-1})(298\text{ K})}{(2.0\text{ L})}$$

= 15.3 atm

(ii) The reaction is $C + \frac{1}{2}O_2 \longrightarrow CO$

According to the equation, 1 mole of CO will be produced for every 1/2 mole of O_2 used.

$\frac{1}{2}$ mol of O_2 gives CO = 1 mol

1.25 mol of O_2 will give CO = 1 × 2 × 1.25
= 2.50 mol

$\therefore$ Final pressure,

$$P = \frac{(2.50\text{ mol})\times(0.0821\text{ L atm K}^{-1})\times(298\text{ K})}{(2.0\text{ L})}$$

= 30.6 atm

20. In 100 g of air,

$$\text{Moles of } N_2 (n_{N_2}) = \frac{w}{\text{Molar mass}} = \frac{75.5}{28} = 2.7$$

$$\text{Moles of } O_2 (n_{O_2}) = \frac{23.2}{32} = 0.725$$

$$\text{Moles of Ar } (n_{Ar}) = \frac{1.3}{40} = 0.0325$$

Total moles = 2.7 + 0.725 + 0.0325 = 3.4575

$$\text{Mole fraction of } N_2 \ (x_{N_2}) = \frac{2.7}{3.4575} = 0.781$$

$$\text{Mole fraction of } O_2 (x_{O_2}) = \frac{0.725}{3.4575} = 0.209$$

$$\text{Mole fraction of Ar } (x_{Ar}) = \frac{0.0325}{3.4575} = 9.39\times10^{-3}$$

$$p_{N_2} = P_{total} \times x_{N_2} = 1\times0.781 = 0.781\text{ bar}$$

$$p_{O_2} = P_{total} \times x_{O_2} = 1\times0.209 = 0.209\text{ bar}$$

$$p_{Ar} = P_{total} \times x_{Ar} = 1\times9.39\times10^{-3} = 9.39\times10^{-3}\text{ bar}$$

21. $n = \frac{370}{32} = 11.56\text{ mol}$

$$V = \frac{nRT}{P} = \frac{11.56\times0.082\times298}{30.0} = 9.416\text{ L}$$

The final number of moles

$$n = \frac{PV}{RT} = \frac{1.0\text{ atm}\times9.43}{0.082\times348} = 0.330\text{ mole}$$

Final weight of O_2 = 0.330 mol × 32 g mol^{-1} = 10.57 g

Mass of O_2 escaped = 370 g (initial) – 10.57 g (final)
= 359.43 g

22. $b = 4\ V$ where V = volume of oxygen gas molecule

or $\quad V = \frac{b}{4} = \frac{0.0318}{4} = 7.95\times10^{-3}\text{ L mol}^{-1}$
$= 7.95\text{ cm}^3\text{ mol}^{-1}$

$\therefore$ Volume occupied by one O_2 molecule

$$= \frac{7.95}{6.02\times10^{23}} = 1.32\times10^{-23}\text{ cm}^3$$

Considering the molecule to be spherical,

$$\frac{4}{3}\pi r^3 = 1.32\times10^{-23} \quad \text{or} \quad r^3 = 3.15\times10^{-24}$$

where r = radius of oxygen atom when oxygen molecule is considered to be spherical

$\therefore$ 3 log r = (log 3.15 ×10^{-24}) = – 24 + 0.4983
= – 23.5017

or $\log r = -7.8339 = \bar{8}.166$

$r = \text{Antilog } \bar{8}.1661 = 1.466 \times 10^{-8}$ cm

$\therefore$ Diameter of oxygen molecule $= 2 \times r$

$= 2 \times 1.466 \times 10^{-8}$ cm $= 2.932 \times 10^{-8}$ cm

$= 2.932$Å

23. (i) Whenever we have a choice between convenience and exercise to burn calories, we should prefer to do the latter.

(ii) Work done by the two students going from ground floor to 4th floor (say) is different as work is a path function.

(iii) By doing work in going by steps, the work is done at the cost of energy, *i.e.*, some calories are burnt. Hence, he or she feels fresh. Here, 1st law of thermodynamics is applicable because one form of energy is converted into equivalent amount of another form.

24. (i) Number of moles of oxygen gas present initially

in the cylinder $= \dfrac{160\text{ g}}{32\text{ g mol}^{-1}} = 5$ moles

To calculate the number of moles now present,

$P = 1.2$ atm, $T = 298$ K, $V = 20.0$ L

Applying the relation, $PV = nRT$, we have,

$$n = \frac{PV}{RT} = \frac{1.2\text{ atm} \times 20.0\text{ L}}{0.0821\text{ L atm K}^{-1}\text{ mol}^{-1} \times 298\text{ K}}$$

$= 0.98$ mol

$\therefore$ Number of moles of O_2 required to be released $= 5 - 0.98 = 4.02$ mol

or Mass of O_2 required to be released

$= 4.02 \times 32 = 128.64$ g

(ii) (a) For ideal gas, $Z = 1$

(b) For a real gas, above Boyle's temperature, gas shows positive deviation and hence $Z > 1$.

OR

(i) Radius of the balloon = 10 m

$\therefore$ Volume of the balloon

$$= \frac{4}{3}\pi r^3 = \frac{4}{3} \times \frac{22}{7} \times (10\text{ m})^3 = 4190.5\text{ m}^3$$

Volume of He filled at 1.66 bar and 27°C

$= 4190.5\text{ m}^3$

Calculation of mass of He :

$$PV = nRT = \frac{w}{M}RT \text{ or } w = \frac{MPV}{RT}$$

$$= \frac{(4 \times 10^{-3}\text{ kg mol}^{-1})(1.66\text{ bar})(4190.5 \times 10^3\text{ dm}^3)}{(0.083\text{ bar dm}^3\text{K}^{-1}\text{ mol}^{-1})(300\text{ K})}$$

$= 1117.5$ kg

Total mass of the balloon along with He

$= 100 + 1117.5 = 1217.5$ kg

Maximum mass of the air that can be displaced by balloon to go up = Volume $\times$ Density

$= 4190.5\text{ m}^3 \times 1.2\text{ kg m}^{-3} = 5028.6$ kg

$\therefore$ Pay load $= 5028.6 - 1217.5$ kg $= 3811.1$ kg

(ii) $PV = nRT$ or $V = \dfrac{nRT}{P} = \dfrac{w}{M}\dfrac{RT}{P}$ $\left(\because n = \dfrac{w}{M}\right)$

$$\therefore V = \frac{8.8\text{ g}}{44\text{ g mol}^{-1}} \times \frac{0.083\text{ bar LK}^{-1}\text{ mol}^{-1} \times (304.1\text{ K})}{1\text{ bar}}$$

$= 5.05$ L

25. (i) As work is being done against constant external pressure, the process is irreversible. Hence,

$w = -P_{ext}\,\Delta V = -2.5\text{ atm} \times (6-4)\text{ dm}^3$

$= -5.0$ L atm ($1\text{dm}^3 = 1$ L)

$= -5.0 \times 101.3$ J $= -506.5$ J (1 L atm = 101.3 J)

For isothermal expansion of ideal gas, $\Delta U = 0$ so that $q = -w = 506.5$ J.

This heat is used up to heat 1 mole of water.

Applying the relation, $q = m \times c \times \Delta T$

$506.5 = 18 \times 4.184 \times \Delta T$

or $\Delta T = 6.725$

$\therefore$ Final temperature $= 20 + 6.725 = 26.725$°C

(ii) Since, the given process is in equilibrium, $\Delta G = 0$

Putting this value in the relationship,

$\Delta G = \Delta H - T\Delta S$

$0 = \Delta H - T\Delta S$ or $T\Delta S = \Delta H$ or $\Delta S = \dfrac{\Delta H}{T}$

Given : $\Delta H = 6.00\text{ kJ mol}^{-1} = 6000\text{ J mol}^{-1}$ and $T = 0°C = 273$ K

$$\therefore \Delta S = \frac{6000\text{ J mol}^{-1}}{273\text{ K}} = 21.98\text{ J K}^{-1}\text{ mol}^{-1}$$

OR

(i) Enthalpy change for the conversion of 1 mole of liquid water at 10°C into 1 mole liquid water at 0°C,

1 mol $H_2O_{(l)}$ at 10°C $\longrightarrow$ 1 mol $H_2O_{(l)}$ at 0°C

$\Delta H_1 = C_p[H_2O_{(l)}] \times \Delta T = -75.3\text{ J mol}^{-1}\text{K}^{-1} \times 10\text{ K}$

$= -753\text{ J mol}^{-1}$

Enthalpy of fusion, $\Delta H_2 = -\Delta H_{freezing}$

$= -6.03\text{ kJ mol}^{-1}$

1 mol $H_2O_{(l)}$ at 0°C $\longrightarrow$ 1 mol $H_2O_{(s)}$ at 0°C

Enthalpy change for the conversion of 1 mole of ice at 0°C to 1 mole of ice at –10°C,

1 mol $H_2O_{(s)}$ at 0°C $\longrightarrow$ 1 mol $H_2O_{(s)}$ at –10°C

$\Delta H_3 = C_p[H_2O_{(s)}] \times \Delta T$

$= -36.8\ \text{J mol}^{-1}\ \text{K}^{-1} \times 10\ \text{K} = -368\ \text{J mol}^{-1}$

$\Delta H_{\text{total}} = -\ (0.753 + 6.03 + 0.368)\ \text{kJ mol}^{-1}$

$= -\ 7.151\ \text{kJ mol}^{-1}$

(ii) The given diagram represents that the process is carried out in infinite steps hence, it is isothermal reversible expansion of the ideal gas from pressure 2.0 atm to 1.0 atm at 298 K.

$$w = -2.303\, nRT \log \frac{p_1}{p_2}$$

$$w = -2.303 \times 1\ \text{mol} \times 8.314\ \text{JK}^{-1}\ \text{mol}^{-1} \times 298\ \text{K} \times \log 2$$

$$\left(\because \frac{p_1}{p_2} = \frac{2}{1}\right)$$

$w = -1717.46$ J

26. $CH_3OH_{(l)} \rightarrow CH_3OH_{(g)}$; $\Delta_{vap}H = 38\ \text{kJ mol}^{-1}$

$\frac{1}{2}H_{2(g)} \rightarrow H_{(g)}$; $\Delta H = 218\ \text{kJ mol}^{-1}$

$2H_{2(g)} \rightarrow 4H_{(g)}$; $\Delta H = (218 \times 4)\text{kJ mol}^{-1}$

$C_{(graphite)} \rightarrow C_{(g)}$; $\Delta H = 715\ \text{kJ mol}^{-1}$

$\frac{1}{2}O_{2(g)} \rightarrow O_{(g)}$; $\Delta H = 249\ \text{kJ mol}^{-1}$

$C{-}H_{(g)} \rightarrow C_{(g)} + H_{(g)}$; $\Delta H = 415\ \text{kJ mol}^{-1}$

$C{-}O_{(g)} \rightarrow C_{(g)} + O_{(g)}$; $\Delta H = 356\ \text{kJ mol}^{-1}$

$O{-}H_{(g)} \rightarrow O_{(g)} + H_{(g)}$; $\Delta H = 463\ \text{kJ mol}^{-1}$

$$C_{(s)} + 2H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow CH_3OH_{(g)}$$

Total energy required is

$(218 \times 4) + 715 + 249 = 1836\ \text{kJ mol}^{-1}$

```
    H
    |
H—C—O—H
    |
    H
```

The following bonds are formed :

Three C—H bonds, one C—O bond, and one O—H bond. Total energy released is :

$(3 \times 415) + 356 + 463 = 2064\ \text{kJ mol}^{-1}$

Net energy released for $CH_3OH_{(g)} = 2064 - 1836$

$= 228\ \text{kJ mol}^{-1}$

For $CH_3OH_{(l)}$ another 38 kJ is released.

Net energy released for $CH_3OH_{(l)} = 228 + 38$

$= 266\ \text{kJ mol}^{-1}$

Therefore,

$\Delta_f HCH_3OH_{(l)} = -266\ \text{kJ mol}^{-1}$

OR

(i) $\Delta G = \Delta H - T\Delta S$ or, $0 = \Delta H - T\Delta S$

$$\text{or}\quad T = \frac{\Delta H}{\Delta S} = \frac{30.56\ \text{kJ mol}^{-1}}{6.6\ \text{JK}^{-1}\text{mol}^{-1}} = 4630\ \text{K}$$

(i) At 4630 K; $\Delta G = 0$

$\therefore$ Reaction is in equilibrium.

(ii) At a temperature below 4630 K,

$\Delta H > T\Delta S$

$\Delta G = \Delta H - T\Delta S$ = positive

$\therefore$ The reaction is non-spontaneous in forward direction, *i.e.*, the reaction occurs in the backward direction. *i.e.*,

$$2Ag_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow 2Ag_2O_{(s)}$$

(ii) Given : V_1 = 1 litre, V_2 = 10 litre,

$T = 273 + 27 = 300$ K, n = 1 mole

$$w = -2.303\ nRT \log \frac{V_2}{V_1}$$

$$= -2.303 \times 1 \times 8.314 \times 300 \log \frac{10}{1}$$

$= -5744.14$ joule.

MPP-3 MONTHLY Practice Problems

Class XI

This specially designed column enables students to self analyse their extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer.
Self check table given at the end will help you to check your readiness.

States of Matter | Chemical Bonding and Molecular Structure

Total Marks : 120 **Time Taken : 60 Min.**

NEET / AIIMS

Only One Option Correct Type

1. At a pressure of 760 torr and a temperature of 273.15 K, the indicated volume of which system is not consistent with the given observations?
   (a) 14 g of N_2 + 16 g of O_2 ; volume = 22.4 L
   (b) 4 g of He + 44 g of CO_2; volume = 44.8 L
   (c) 7 g of N_2 + 36 g of O_3 ; volume = 22.4 L
   (d) 17 g of NH_3 + 36.5 g of HCl, volume = 44.8 L

2. Helium gas at 1 atm and SO_2 at 2 atm pressure, temperature being the same, are released separately at the same moment into 1m long evacuated tubes of equal diameters. If helium reaches the other end of the tube in *t* s, what distance SO_2 would traverse in the same time interval in the other tube?
   (a) 25 cm (b) 50 cm
   (c) 60 cm (d) 75 cm

3. Increasing order of dipole moments is given by
   (a) $CF_4 < NH_3 < NF_3 < H_2O$
   (b) $CF_4 < NH_3 < H_2O < NF_3$
   (c) $CF_4 < NF_3 < H_2O < NH_3$
   (d) $CF_4 < NF_3 < NH_3 < H_2O$

4. Consider the following statements :
   I. Bond length in N_2^+ is 0.02 Å greater than that in N_2.
   II. Bond length in NO^+ is 0.09 Å less than that in NO.
   III. O_2^{2-} has a shorter bond length than O_2.
   Which of the given statements are correct?
   (a) I and II (b) II and III
   (c) I and III (d) All of these

5. A perfect gas of a given mass is heated first in a small vessel and then in a large vessel, such that their volume remains unchanged. The *P*-*T* curves are
   (a) parabolic with same curvature
   (b) parabolic with different curvature
   (c) linear with same slope
   (d) linear with different slopes.

6. For the equation, $\left[P_r + \dfrac{3}{V_r^2}\right][3V_r - 1] = 8T_r$
   the correct statement is that
   (a) the equation is for law of corresponding states.
   (b) the equation states 'under similar conditions of reduced pressure (P_r) and reduced temperature (T_r) gases possess same reduced volume (V_r)'
   (c) the equation provides better results at boiling point of two liquids
   (d) all of the above.

7. The paramagnetic property of the oxygen molecule is due to the presence of unpaired electrons present in
   (a) $(\sigma 2p_x)^1$ and $(\sigma^* 2p_x)^1$
   (b) $(\sigma 2p_x)^1$ and $(\pi 2p_y)^1$
   (c) $(\pi^* 2p_y)^1$ and $(\pi^* 2p_z)^1$
   (d) $(\pi^* 2p_y)^1$ and $(\pi 2p_y)^1$

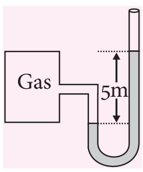
8. The common features among the species CN^-, CO and NO^+ are
   (a) bond order three and isoelectronic
   (b) bond order three and weak field ligands

(c) bond order two and π-acceptors
(d) isoelectronic and weak field ligands.

9. A spherical air bubble is rising from the depth of a lake when pressure is P atm and temperature is T K. The percentage increase in its radius when it comes to the surface of a lake will be : (Assume temperature and pressure at the surface to be respectively $2T$ K and P / 4)
(a) 100% (b) 50% (c) 40% (d) 200%

10. The correct order of hybridization of the central atom in the following species NH_3, $[PtCl_4]^{2-}$, PCl_5 and BCl_3 is
(a) dsp^2, dsp^3, sp^2 and sp^3
(b) sp^3, dsp^2, sp^3d, sp^2
(c) dsp^2, sp^2, sp^3, dsp^3
(d) dsp^2, sp^3, sp^2, dsp^3

11. A gas jar of 10 litre volume filled with O_2 at 300 K is connected to glycerine manometer. The manometer shows 5 m difference in the level as shown in figure. What will be the number of moles of O_2 in the gas jar ?



(Given $d_{glycerine}$ = 2.72 g/mL; $d_{mercury}$ = 13.6 g/mL)
(a) 0.64 mol (b) 0.4 mol
(c) 0.94 mol (d) 0.36 mol

12. Which of the following represents the correct order of Cl–O bond lengths in ClO^-, ClO_2^-, ClO_3^-, ClO_4^- ?
(a) $ClO_4^- = ClO_3^- = ClO_2^- = ClO^-$
(b) $ClO^- < ClO_2^- < ClO_3^- < ClO_4^-$
(c) $ClO_4^- < ClO_3^- < ClO_2^- < ClO^-$
(d) $ClO_3^- < ClO_4^- < ClO_2^- < ClO^-$

Assertion & Reason Type

Directions : In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :
(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

13. Assertion : A closed cylinder containing high pressure gas tends to rise against gravity when the gas is allowed to escape through an orifice at the bottom.
Reason : The velocity of escaping gas develops an upward thrust proportional to the area of cross-section of the orifice.

14. Assertion : Fluorine molecule has bond order one.
Reason : The number of electrons in the antibonding molecular orbitals is two less than that in bonding molecular orbitals.

15. Assertion : Compressibility factor (Z) for non-ideal gases is always greater than 1.
Reason : Non-ideal gases always exert higher pressure than expected

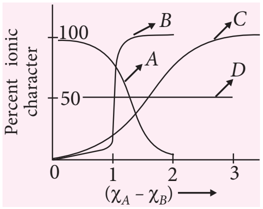
JEE MAIN / JEE ADVANCED / PETs

Only One Option Correct Type

16. Potassium hydroxide solutions are used to absorb CO_2. How many litres of CO_2 at 1.00 atm and 22°C would be absorbed by an aqueous solution containing 15.0 g of KOH?
$2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$
(a) 3.24 L (b) 1.62 L
(c) 6.48 L (d) 0.324 L

17. A large cylinder of helium filled at 1000 pascal had a small thin orifice through which helium escaped into an evacuated space at the rate of 6.4 mmol/h. How long will it take for 10 mmol SO_2 to leak through a similar orifice if the SO_2 were confined at the same pressure?
(a) 6.25 h (b) 0.39 h
(c) 4.42 h (d) 1.00 h

18. For AB bond if percent ionic character is plotted against electronegativity difference $(\chi_A - \chi_B)$, the shape of the curve would look like



(a) A (b) B (c) C (d) D

19. The bond dissociation energy of B—F in BF_3 is 646 kJ mol^{-1} whereas that of C—F in CF_4 is 515 kJ mol^{-1}. The correct reason for higher B—F bond dissociation energy as compared to that of C—F is

(a) smaller size of B-atom as compared to that of C-atom.

(b) stronger σ-bond between B and F in BF_3 as compared to that between C and F in CF_4.

(c) significant $p\pi$–$p\pi$ interaction between B and F in BF_3 whereas there is no possibility of such interaction between C and F in CF_4.

(d) lower degree of $p\pi$–$p\pi$ interaction between B and F in BF_3 than that between C and F in CF_4.

More than One Options Correct Type

20. For two gases A and B with molecular weights M_A and M_B, respectively, it is observed that at a certain temperature T, the mean velocity of A is equal to the V_{rms} of B. Thus, the mean velocity of A can be made equal to the mean velocity of B, if

(a) A is at temperature T and B is at T' such that $T > T'$

(b) temperature of A is lowered to T_2 while B is at T such that $T_2 < T$

(c) both A and B are raised to a higher temperature

(d) heat energy is supplied to A.

21. If 10 g of a gas at atmospheric pressure is cooled from 273°C to 0°C keeping the volume constant, its pressure would become

(a) 1/273 atm (b) 2 atm

(c) $\frac{1}{2}$ atm (d) 5.05×10^4 Nm^{-2}

22. The molecules that will have dipole moment are
(a) 2,2-dimethylpropane
(b) *trans*-2-pentene (c) *cis*-3-hexene
(d) 2,2,3,3-tetramethylbutane.

23. The molecules or ions which have bond pairs as well as lone pairs of electrons on the central atom are
(a) SF_4 (b) ClF_3 (c) XeF_2 (d) CO_3^{2-}

Integer Answer Type

24. To an evacuated vessel with movable piston under external pressure of 1 atm, 0.1 mol of He and 1.0 mol of an unknown compound (vapour pressure 0.68 atm at 0°C) are introduced. Considering the ideal gas behaviour, the total volume (in litres) of the gases at 0°C is close to

25. The number of molecules among the following which do not satisfy octet rule is
$BeCl_2$, $AlCl_3$, H_2O_2, H_2SO_4, HNO_3, SO_3, PCl_5, CO_2, CO, O_3, $HClO_4$, NO_2^-

26. Equal masses of O_2 and SO_2 gases were mixed in a vessel of 5 L capacity at 20°C. The total pressure exerted by the mixture was recorded to be 12 atm. The pressure exerted by O_2 in atmosphere is

Comprehension Type

The phenomena of diffusion and effusion are very common in our everyday life. The smell of food cooked in the kitchen spreads in the whole house. It is diffusion. Air from tyre or gas from cylinder leaks out. It is effusion. Thomas Graham studied the rates at which diffusion or effusion takes place. He studied the effect of the nature of the gas, temperature and pressure on the rates of diffusion/effusion and put forward exact mathematical relations giving the effect of these parameters on the rates of diffusion/effusion.

27. According to Graham's law at a given temperature, the ratio of the rates of diffusion r_A/r_B of gases A and B is given by
(a) $(P_A/P_B)\,(M_A/M_B)^{1/2}$ (b) $(M_A/M_B)\,(P_A/P_B)^{1/2}$
(c) $(P_A/P_B)(M_B/M_A)^{1/2}$ (d) $(M_A/M_B)\,(P_B/P_A)^{1/2}$

28. Through the two ends A and B of a glass tube of length 1 metre, hydrogen chloride and ammonia gas are allowed to enter from ends A and B respectively. The white fumes of ammonium chloride will appear from end A at a distance of approximately
(a) 60 cm (b) 40 cm (c) 68 cm (d) 32 cm

Matrix Match Type

29. Match the entries listed in column I with appropriate entries listed in column II.

Column I	Column II
(A) Hydrogen gas (P = 200 atm, T = 273 K)	(P) Compressibility factor ≠ 1
(B) Hydrogen gas (P = 0, T = 273 K)	(Q) Attractive forces are dominant
(C) CO_2 (P = 1 atm, T = 273 K)	(R) $PV = nRT$
(D) Real gas with large molar volume	(S) $P(V - nb) = nRT$

	A	B	C	D
(a)	Q, S	P, R	P, Q	S, P
(b)	P, S	R	P, Q	R
(c)	P, R	P	Q, S	P, R, Q
(d)	P, R	P, Q, S	P	Q, S

30. Match the entries listed in column I with appropriate entries listed in column II.

Column I	Column II
(A) B_2	(P) Paramagnetic
(B) N_2	(Q) Undergoes oxidation
(C) O_2^-	(R) Undergoes reduction
(D) O_2	(S) Bond order ≥ 2
	(T) Mixing of s and p-orbitals

	A	B	C	D
(a)	P, R, T	S, T	P, Q	P, Q, S
(b)	P, Q, S	S, T	P, Q	P, R, T
(c)	P, R, T	P, Q	S, T	P, Q, S
(d)	P, Q, S	P, Q	S, T	P, R, T

◇◇

Keys are published in this issue. Search now! ☺

SELF CHECK

No. of questions attempted ……
No. of questions correct ……
Marks scored in percentage ……

Check your score! If your score is

> 90%	EXCELLENT WORK !	You are well prepared to take the challenge of final exam.
90-75%	GOOD WORK !	You can score good in the final exam.
74-60%	SATISFACTORY !	You need to score more next time.
< 60%	NOT SATISFACTORY!	Revise thoroughly and strengthen your concepts.

CONCEPT MAP

Class XI | Class XII

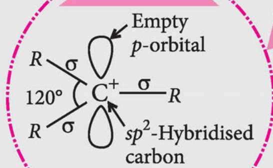
REACTIVE INTERMEDIATES

Intermediates which are short-lived species generated during conversion of reactants to products in a chemical reaction. They play an important role in various organic synthesis as well as in biological world.

Carbocation ($\rightarrow\!C^+$)

Carbon species carrying +ve charge on carbon having only six electrons in its valence shell.

Structure



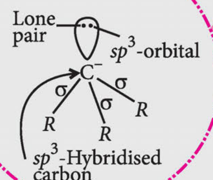
Stability

- More the number of alkyl/aryl groups present, greater is the stability.
- Electron donating groups increase the stability whereas electron withdrawing groups decrease the stability.
- The decreasing order of the stabilities of carbocations :
  $(Ph)_3\overset{+}{C} \approx (R)_2\overset{+}{C}\text{–}CH{=}CH_2 > (Ph)_2\overset{+}{C}H \approx R\overset{+}{C}HCH{=}CH_2 > R_3C^+ > Ph\overset{+}{C}H_2 >$
  $(R)_2\overset{+}{C}H > \overset{+}{C}H_2CH{=}CH_2 > R\overset{+}{C}H_2 > \overset{+}{C}H_3 > \overset{+}{C}H{=}CH_2 > \overset{+}{Ph}$ or $\overset{+}{Ar}$

Carbanion ($\rightarrow\!\bar{C}:$)

Carbon species carrying –ve charge on carbon having eight electrons in its valence shell.

Structure



Stability

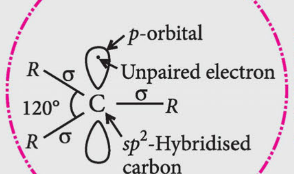
- More the number of alkyl groups present, lower is the stability.
- Electron withdrawing groups increase stability whereas electron donating groups decrease stability.
- The order of stability of carbanions :
  $(C_6H_5)_2CH^- > (C_6H_5)_3\bar{C} > C_6H_5\bar{C}H_2 > \text{allyl} > \bar{C}H_3 >$ 1°alkyl > 2°alkyl > 3°alkyl

Note : Carbanions are sp^3-hybridised with pyramidal geometry. Due to steric hindrance of three phenyl (Ph–) groups, and to acquire pyramidal geometry, lots of energy is required due to which Ph_3C^- is less stable than Ph_2CH^-.

Free Radical ($\rightarrow\!\dot{C}$)

Atom or a group of atoms having odd or unpaired electron having seven electrons in its valence shell. They are highly unstable, electrically neutral and short-lived species.

Structure



Stability

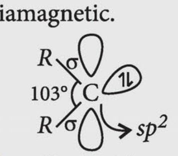
- More the number of alkyl groups present, greater is the stability.
- Allyl and benzyl free radicals are more stable than alkyl free radicals due to resonance effect.
- Greater the number of phenyl groups, more stable is the free radical.
- The order of the stability of free radicals is
  $(C_6H_5)_3\dot{C} > (C_6H_5)_2\dot{C}H > C_6H_5\dot{C}H_2 > CH_2{=}\dot{C}HCH_2 >$
  $3°\text{alkyl} > 2°\text{alkyl} > 1°\text{alkyl} > \dot{C}H_3 > CH_2{=}\dot{C}H > HC{\equiv}\dot{C}$

Carbene (:CH₂)

Neutral, divalent carbon species in which two non-bonding electrons are present along with two bonding pairs (*i.e*; having sextet of electrons)

Singlet

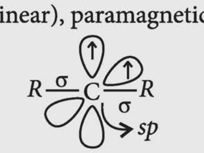
sp^2-hybridised (bent), diamagnetic.



Electrophile

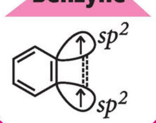
Triplet

sp-hybridised (linear), paramagnetic



Diradical (more stable)

Benzyne

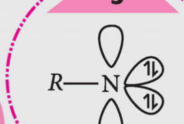


An additional bond is formed between two neighbouring carbon atoms by side ways overlapping of two sp^2-orbitals. The new bond orbital lies along with side of the ring and has little interaction with the π-electron cloud lying above and below the ring. This sideways overlapping is weak and thus, makes the benzyne more reactive.

Nitrenes or Imidogens ($R - \ddot{N}$)

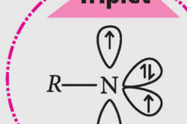
Neutral, univalent nitrogen species in which nitrogen has a sextet of electrons. They are highly reactive and act as strong electrophiles

Singlet



Electrophile

Triplet



Diradical

SOME COMMERCIAL CELLS (BATTERIES)

Batteries are cleverly engineered devices that are based on the same fundamental laws as galvanic cells. A storage cell is a galvanic cell that contains all the reactants needed to produce electricity whereas fuel cell is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity.

PRIMARY CELLS

Cells once exhausted cannot be used again therefore, they are not chargeable.

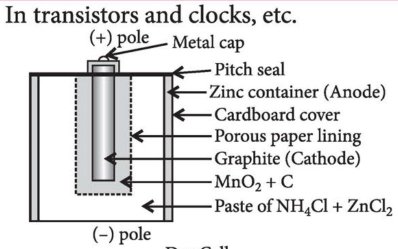
DRY CELL

Anode : $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

Cathode : $2NH^+_{4(aq)} + 2MnO_{2(s)} + 2e^- \rightarrow 2MnO(OH) + 2NH_3$

Net reaction : $Zn_{(s)} + 2NH^+_{4(aq)} + 2MnO_{2(s)} \rightarrow Zn^{2+}_{(aq)} + 2MnO(OH) + 2NH_3$

Uses : In transistors and clocks, etc.



Dry Cell

MERCURY CELL (Ruben-Mallory Cell)

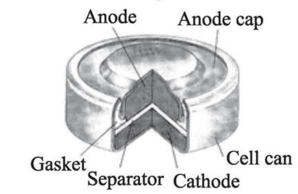
Anode : $Zn(Hg) + 2OH^-_{(aq)} \rightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^-$

Cathode : $HgO_{(s)} + H_2O_{(l)} + 2e^- \rightarrow Hg_{(l)} + 2OH^-_{(aq)}$

Net reaction : $Zn(Hg) + HgO_{(s)} \rightarrow ZnO_{(s)} + Hg_{(l)}$

The cell potential is approximately 1.35 V and remains constant during its life.

Uses : In watches, hearing aids, etc.



Mercury cell

(The reducing agent is zinc and the oxidising agent is mercury (II) oxide.)

SECONDARY CELLS

Cells which can be used again and again therefore, they are chargeable.

LEAD STORAGE CELL

Cell reactions during use of battery :

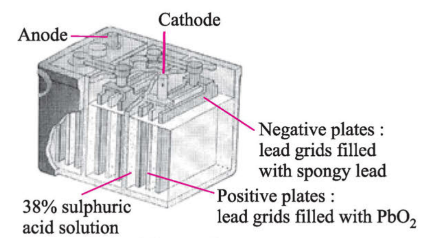
Anode : $Pb_{(s)} + SO^{2-}_{4(aq)} \rightarrow PbSO_{4(s)} + 2e^-$

Cathode : $PbO_{2(s)} + SO^{2-}_{4(aq)} + 4H^+_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$

Net reaction :
$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$

The reverse reaction takes place during recharging :
$2PbSO_{4(s)} + 2H_2O_{(l)} \rightarrow Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)}$

Uses : In automobiles and inverters.



Lead Storage Battery

NICKEL - CADMIUM CELL (or NICAD cell)

Cell reactions during use of battery :

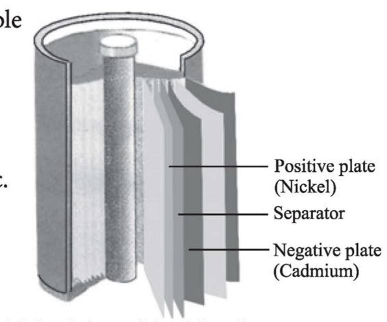
Cathode : $2Ni(OH)_{3(s)} + 2e^- \rightarrow 2Ni(OH)_{2(s)} + 2OH^-_{(aq)}$

Anode : $Cd_{(s)} + 2OH^-_{(aq)} \rightarrow CdO_{(s)} + H_2O_{(l)} + 2e^-$

Net reaction : $Cd_{(s)} + 2Ni(OH)_{3(s)} \rightarrow CdO_{(s)} + 2Ni(OH)_{2(s)} + H_2O_{(l)}$

The reverse reaction takes place during recharging :
$CdO_{(s)} + 2Ni(OH)_{2(s)} + H_2O_{(l)} \rightarrow Cd_{(s)} + 2Ni(OH)_{3(s)}$

Uses : In portable electronic devices, emergency lighting, photography equipments, etc.



A rechargeable nickel-cadmium cell in a jelly roll arrangement and separated by a layer soaked in moist sodium or potassium hydroxide.

FUEL CELLS

Cells which can convert the energy of combustion of fuels such as H_2, CO, CH_4 etc. into electrical energy.

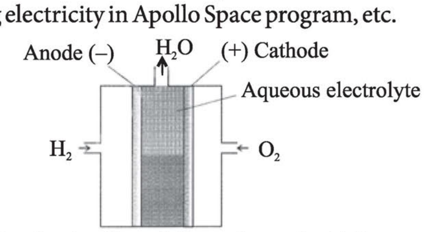
$H_2 - O_2$ FUEL CELL

Anode : $2H_{2(g)} + 4OH^-_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^-$

Cathode : $O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$

Net reaction : $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$

Uses : In automobiles on experimental basis, for producing electricity in Apollo Space program, etc.



Fuel cell using H_2 and O_2 produces electricity.

CLASSIFICATION OF FUEL CELLS

(i) Alkali fuel cells [electrolyte is $KOH_{(aq)}$] (ii) Phosphoric acid fuel cells [electrolyte is $H_3PO_{4(aq)}$]. (iii) Molten carbonate fuel cells [electrolyte is $K_2CO_{3(l)}/Li_2CO_{3(l)}$] here, methane is used as a fuel. Recently, a zinc-air fuel cell (ZAFC) is developed in USA as a source of power in automobiles in which zinc metal is used in place of hydrogen gas.

NEET | JEE ESSENTIALS

Class XII

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Unit 3

GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS
p-BLOCK ELEMENTS (Group 15 to 18)

GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS

- A few elements like carbon, sulphur, gold and noble gases, occur in free state while others in combined forms in the earth's crust. The extraction and isolation of an element from its combined form involves various principles of chemistry.

Metallurgy

- The entire scientific and technological processes used for isolation of metal from its ores is called *metallurgy*.

Elements — **Modes of occurrence** — **Metals**

Native state
Least reactive elements like noble gases and noble metals occur in free state or native state.
Combined state
Highly reactive elements like fluorine, chlorine, sodium, etc. are found in combined state.

Minerals
Naturally occurring chemical substances in the earth's crust obtainable by mining.
Ores
The minerals from which we can obtain metal profitably and easily.

Metallurgical Processes

- **Crushing and grinding of the ore :** Involves the breaking of huge lumps into small pieces using crushers or grinders which in turn reduced to fine powder using ball or stamp mill.
- **Concentration of ore :** Involves the removal of gangue from ore.

➢ The different methods used in this process are :

Based on nature of ores and impurities present

Hydraulic washing : Based on the difference in the specific gravities of the gangue and the ore particles. Therefore, heavier ore particles settle down while lighter impurities are washed away. For example, oxide ores like haematite, tinstone and native ores of Au, Ag, etc.

Electromagnetic separation : Based on the difference in magnetic properties of the gangue and ore particles. Therefore, magnetic particles fall nearer to the roller while non-magnetic particles fall farther off. For example, magnetite (Fe_3O_4), haematite (Fe_2O_3), wolframite ($FeWO_4$), chromite ($FeO \cdot Cr_2O_3$), etc.

Froth floatation process : Based on the difference in wetting properties of gangue and ore particles. Therefore, ore particles rise to the surface in the form of froth and impurities remain in water. For example, sulphide ores.

Leaching : Based on the difference in chemical properties of gangue and ore particles. Used for extraction of Au, Ag (*Mac Arthur Forest cyanide process*) and pure alumina from bauxite ore (*Baeyer's process*).

➢ **Extraction and isolation of metals :** Involves extraction of metal in free state from concentrated ore. The following two chemical processes used are :

Oxidation or de-electronation process

- **Calcination :** Process of heating the ore strongly below its melting point either in the absence of air or in the limited supply. *e.g.*, carbonate and hydrated oxide ores.
- **Roasting :** Process of heating the ore strongly below the melting point in a sufficient supply of air to bring about its oxidation and remove volatile impurities. *e.g.*, sulphide ores.

Reduction process

Reduction of calcinated or roasted ore to metal using reducing agent. For *example*,

- Carbon or carbon monoxide is used for oxides of Fe, Cu, Zn, Mg, Co, etc.
- Electropositive metals like Na, Al, Mg or hydrogen are used for reduction of ores of Mn, Cr, Ti, Mo, W, etc.
- Water gas is used for nickel ores.
- Auto-reduction process is used for ores of Pb, Hg, Cu, etc.
- Electrolytic reduction is used for highly electropositive metals.
- Hydrometallurgy or displacement method is used for Ag, Au, etc.

INFO SHOTS

Extraction of cleaner copper with energy capture!

In February 2016, a toxin-free method for extraction of copper from raw ore and other procedures using molten salts have been developed. Recent method involves the chemical processes that produce huge mountains of waste mine tailings and lake-size waste water collections, accumulating high levels of toxins such as arsenic, cadmium and sulphuric acid. But latest method works by heating ore using molten salts to temperatures exceeding 1500°F such that copper is separated from the ore without use of water and dangerous chemicals. The technology also allows for the collection of surplus heat and using it to power steam turbines and generators. These technologies could really shift the paradigm with cleaner, more efficient methods for both mining and energy storage.

➢ **Refining of metals :** Involves the purification of crude metals by removing the impurities present in it.

➤ The different methods used in this process are :

Based on differences in properties of metals and impurities

Liquation
Used for low melting metals like Sn, Pb, Hg, Bi, etc.

Cupellation
Used for metals containing easily oxidisable impurities. *e.g.*, Ag containing Pb impurities.

Poling
Used for metals which contain impurities of their own oxides, *e.g.*, Cu.

Mond's process
Used for refining of Ni.

$$4CO + \underset{\text{Impure}}{Ni} \xrightarrow{\Delta} Ni(CO)_4\downarrow$$

$$Ni(CO)_4 \xrightarrow{180°C} \underset{\text{Pure}}{Ni} + 4CO$$

Electrolytic refining
Used for metals like Cu, Ag, Au, Al which get deposited at cathode and impurities get deposited at anode. Solution of a soluble metal salt acts as the electrolyte.

van Arkel method
Used for ultra-pure metals like Ti, Zr which are used in space technology.

$$\underset{\text{Impure}}{Ti_{(s)}} + 2I_{2(g)} \xrightarrow{523\text{ K}} TiI_{4(g)} \xrightarrow{1673\text{ K}} \underset{\text{Pure}}{Ti_{(s)}} + 2I_{2(g)}$$

$$\underset{\text{Impure}}{Zr_{(s)}} + 2I_{2(g)} \xrightarrow{870\text{ K}} ZrI_{4(g)} \xrightarrow{1800\text{ K}} \underset{\text{Pure}}{Zr_{(s)}} + 2I_{2(g)}$$

Zone refining
Used to produce extremely pure metals (semiconductors) like Si, Ge, Ga, B and In.

THERMODYNAMIC PRINCIPLES OF METALLURGY

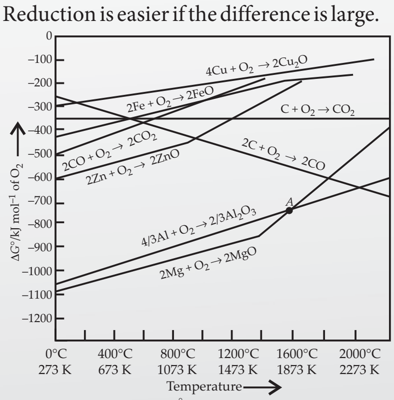
Thermodynamic principles :

- With the help of thermodynamics, the temperature conditions and suitable reducing agents in the metallurgical processes can be decided.
- Gibb's Helmholtz equation ($\Delta G° = \Delta H° - T\Delta S°$), is used to check the feasibility of a reaction.
- $\Delta G° < 0$ (Spontaneous reaction)

Ellingham diagram : The graphical representation of Gibbs free energy change *vs* absolute temperature for a process is known as *Ellingham diagram*.

Salient features

- The $\Delta G°$ *vs* T graphs are straight lines unless the materials melt or vaporise (*i.e.*, change from solid $\rightarrow$ liquid or from liquid $\rightarrow$ gas).
- Metal oxide with lower value of $\Delta G°$ is more stable than a metal oxide with higher $\Delta G°$.
- The coupling or combination of oxidation and reduction reactions helps in interpreting whether the given reducing agent can be useful or not.
- All the $\Delta G°$ *vs* T lines have slopes upwards because $\Delta G°$ becomes less and less negative with increase in temperature.
- The diagram shows that reduction of the oxide of the elements in upper line is feasible by the elements represented by the lower line. Reduction is easier if the difference is large.



Gibbs energy ($\Delta G°$) *vs* T plots for formation of some oxides (Ellingham diagram)

p-BLOCK ELEMENTS (Group 15 to 18)

GROUP 15 ELEMENTS (PNICOGENS)

- **Electronic configuration :** **N(7)** - [He]$2s^2 2p^3$; **P(15)** - [Ne]$3s^2 3p^3$; **As(33)** - [Ar]$3d^{10} 4s^2 4p^3$; **Sb(51)** - [Kr]$4d^{10} 5s^2 5p^3$; **Bi(83)** - [Xe]$4f^{14} 5d^{10} 6s^2 6p^3$

PHYSICAL PROPERTIES

Group 15 Elements (ns^2np^3)

Physical state and metallic character : N_2 (unreactive gas), P_4 (solid non-metal), As_4 and Sb_4 (solid metalloids), Bi (solid metal).

Atomic radii : Increase down the group, smaller than that of group 14 elements due to increased nuclear charge.

Melting and boiling points : M.pt. increases from N to As and then decreases whereas b. pt. increases from N to Sb and decreases very slightly.

Ionisation enthalpy : Decreases regularly down the group due to increase in size.

Electronegativity : Decreases down the group.

Atomicity : Nitrogen (diatomic gaseous molecule), phosphorus, arsenic, antimony (discrete tetratomic tetrahedral molecules).

Thermal and electrical conductivity : Increase down the group, as delocalisation of electrons increases.

Allotropy : Nitrogen (α and β-Nitrogen), phosphorus (white, red, scarlet, violet, α-black, β-black), arsenic (grey, yellow, black) antimony (metallic, yellow, explosive).

CHEMICAL PROPERTIES

Chemical properties

Oxides

Group 15 elements form oxides of type X_2O_3, X_2O_4, X_2O_5
Acidic nature decreases (left to right), increases (down the group)

Oxidation state

Stability of +3 increases and +5 decreases down the group.

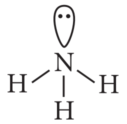
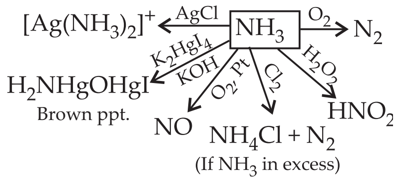
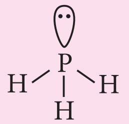
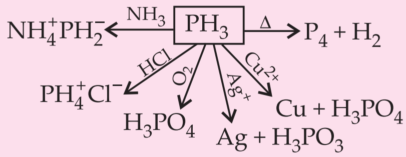
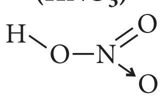
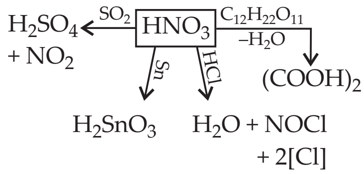
Hydrides

Thermal stability : $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
Solubility : $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
Basic character : $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
Bond angle : $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
Reducing character : $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$
Covalent character : $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

Halides (MX_3 and MX_5)

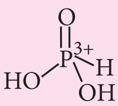
Group 15 elements form MX_3, whereas all form MX_5 except nitrogen.
Stability : $NF_3 > NCl_3 > NBr_3$
Lewis acid strength : $PCl_3 > AsCl_3 > SbCl_3$ and $PF_3 > PBr_3 > PI_3$
Lewis base strength : $NI_3 > NBr_3 > NCl_3 > NF_3$
Bond angle : $PF_3 < PCl_3 < PBr_3 < PI_3$ (increasing *b.p.* – *b.p.* repulsions)

Important Compounds of Nitrogen and Phosphorus

Compounds	Preparations	Properties
Ammonia (NH_3)  sp^3 hybridisation (pyramidal)	**Haber's process :** $N_{2(g)} + 3H_{2(g)} \xrightleftharpoons{773K} 2NH_{3(g)}$ $NH_4Cl + NaOH \longrightarrow NH_3 + H_2O + NaCl$ $2NH_4Cl + \underset{\text{Slaked lime}}{Ca(OH)_2} \xrightarrow{\Delta} CaCl_2 + 2NH_3 + 2H_2O$ $Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$	
Phosphine (PH_3)  sp^3 hybridisation (pyramidal)	$4H_3PO_3 \xrightarrow{478\text{-}483\ K} 3H_3PO_4 + PH_3$ $P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$ $PH_4I + KOH \longrightarrow PH_3 + KI + H_2O$ $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$	
Nitric acid (HNO_3) 	$2KNO_3 + H_2SO_4 \longrightarrow 2HNO_3 + K_2SO_4$ $4NH_{3(g)} + 5O_{2(g)} \xrightarrow[500\ K,\ 9\ bar]{Pt/Rh\ gauge} 4NO_{(g)} + 6H_2O_{(g)}$ $2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$ $3NO_{2(g)} + H_2O_{(l)} \longrightarrow 2HNO_{3(aq)} + NO_{(g)}$	

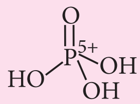
Oxoacids of phosphorus

Phosphonic acid (H_3PO_3)



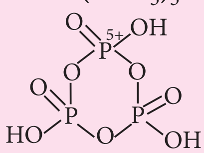
Dibasic and reducing agent

Phosphoric acid (H_3PO_4)



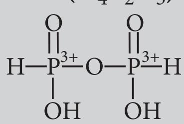
Tribasic and non reducing

Cyclotrimetaphosphoric acid ($(HPO_3)_3$)



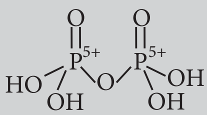
Tribasic

Pyrophosphorous acid ($H_4P_2O_5$)



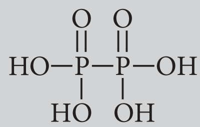
Dibasic and reducing agent

Pyrophosphoric acid ($H_4P_2O_7$)



Tetrabasic

Hypophosphoric acid ($H_4P_2O_6$)



Tetrabasic

GROUP 16 ELEMENTS (CHALCOGENS)

- **Electronic configurations : O(8)** - [He]$2s^2 2p^4$; **S(16)**-[Ne]$3s^2 3p^4$; **Se(34)**-[Ar]$3d^{10} 4s^2 4p^4$; **Te(52)**-[Kr]$4d^{10} 5s^2 5p^4$; **Po(84)**-[Xe]$4f^{14} 5d^{10} 6s^2 6p^4$

Physical Properties

Allotropy : All elements show allotropy

Group 16 Elements (ns^2np^4)

Electronegativity : Decreases down the group.

Electron gain enthalpy : Increases from oxygen to sulphur and then decreases.

Melting and boiling points : Increase down the group upto Te and then decreases.

Physical state and metallic character : O_2 (gas), S_8 (solid non-metal), Se and Te (solid metalloids), Po (radioactive metal)

Atomic radii : Increase down the group.

Ionisation enthalpy : Decreases down the group.

Atomicity : Oxygen (diatomic molecule), S, Se, Te (form polyatomic complex molecules).

Chemical Properties

Chemical properties

Oxidation state

Stability of –2, +6 oxidation states decreases down the group and +4 oxidation state increases down the group.

Hydrides

Boiling point : $H_2O > H_2Te > H_2Se > H_2S$

Volatility : $H_2S > H_2Se > H_2Te > H_2O$

Bond angle : $H_2O > H_2S > H_2Se > H_2Te$

Acidic character : $H_2O < H_2S < H_2Se < H_2Te$

Reducing power : $H_2Te > H_2Se > H_2S > H_2O$

Halides (EX_6, EX_4 and EX_2)

Hexahalides stability: $SF_6 > SeF_6 > TeF_6$

Tetrahalides : SF_4(gas), SeF_4 (liquid), TeF_4 (solid). SF_4 readily hydrolysed than SF_6.

Dihalides : All elements except selenium form dihalides.

Monohalides : Dimeric in nature and undergoes disproportionation.

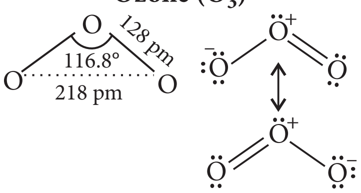
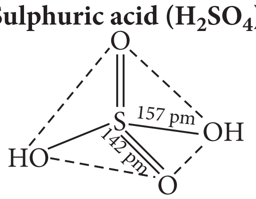
Oxides

Monoxides : Except selenium, all elements form monoxides, *MO*.

Dioxides : All elements form dioxides MO_2, when burnt in air. SO_2 (monomeric), SeO_2 (polymeric), TeO_2 and PoO_2 (ionic solids).

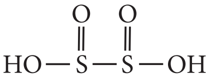
Trioxides : Sulphur, selenium, tellurium form trioxides, MO_3.

Important Compounds of Oxygen and Sulphur

Compounds	Preparation	Properties
Ozone (O_3) 	$3O_2 \xrightleftharpoons{\text{Silent electric discharge}} 2O_3$	$O_3 \xrightarrow{NO} O_2 + NO_2$ $O_3 \xrightarrow{H_2S} H_2O + S + O_2$ $O_3 \xrightarrow{KOH} KO_3$ $O_3 \xrightarrow{PbS} PbSO_4$ $O_3 \xrightarrow{HCl + SnCl_2} SnCl_4$ $O_3 \xrightarrow[H_2O/Zn]{CH_2=CH_2} HCHO$
Sulphuric acid (H_2SO_4)  Sulphuric acid	**Contact process :** $2SO_{2(g)} + O_{2(g)} \xrightarrow{V_2O_5} 2SO_{3(g)}$ $2SO_{3(g)} \xrightarrow{H_2SO_4} H_2S_2O_7$ $H_2S_2O_7 \xrightarrow{H_2O} 2H_2SO_4$	$H_2SO_4 \xrightarrow{NaOH} NaHSO_4 + H_2O$ $H_2SO_4 \xrightarrow{2NaOH} Na_2SO_4 + 2H_2O$ $H_2SO_4 \xrightarrow{Zn} ZnSO_4 + H_2$ $H_2SO_4 \xrightarrow{C_{12}H_{22}O_{11}} 12C + 11H_2O$ $H_2SO_4 \xrightarrow{S_8} SO_2 + H_2O$ $H_2SO_4 \xrightarrow{Na_2S} Na_2SO_4 + H_2S$ $H_2SO_4 \xrightarrow{BaCl_2} BaSO_4 + HCl$ $H_2SO_4 \xrightarrow{K_4[Fe(CN)_6]} K_2SO_4 + FeSO_4 + (NH_4)_2SO_4 + CO\uparrow$

Oxoacids of sulphur

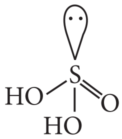
Hyposulphurous acid ($H_2S_2O_4$)



Unstable in pure form but stable as salts.
O.S. of S = +3

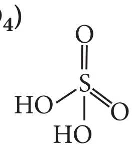
Sulphurous acid (H_2SO_3)

Dibasic acid, strong reducing agent.
O.S. of S = +4



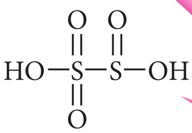
Sulphuric acid (H_2SO_4)

Dibasic acid, strong oxidising and dehydrating agent.
O.S. of S = +6



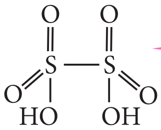
Pyrosulphurous acid or Disulphurous acid ($H_2S_2O_5$)

O.S. of S = +3 and +5



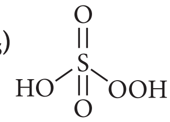
Dithionic acid ($H_2S_2O_6$) :

Dibasic acid
O.S. of S = +5



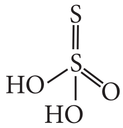
Peroxomonosulphuric acid (Caro's acid) (H_2SO_5)

Monobasic acid, strong oxidising agent.
O.S. of S = +6



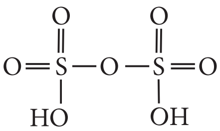
Thiosulphuric acid ($H_2S_2O_3$)

Dibasic acid, reducing agent.
O.S. of S = −2, +6

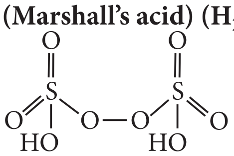


Disulphuric acid or Pyrosulphuric acid ($H_2S_2O_7$)

A sulphuric acid analogue of acetic anhydride.
O.S. of S = +6



Peroxodisulphuric acid (Marshall's acid) ($H_2S_2O_8$)



Dibasic acid, strong oxidising agent.
O.S. of S = +6

GROUP 17 ELEMENTS (HALOGENS)

- **Electronic configuration : F(7)** - [He]$2s^2 2p^5$; **Cl(17)** - [Ne]$3s^2 3p^5$; **Br(35)** - [Ar]$3d^{10} 4s^2 4p^5$; **I(53)** - [Kr]$4d^{10} 5s^2 5p^5$; **At(85)** - [Xe]$4f^{14} 5d^{10} 6s^2 6p^5$

Physical Properties

Group 17 Elements ($ns^2 np^5$)

Heat of hydration : $F^- > Cl^- > Br^- > I^-$

Oxidising power and reactivity $F_2 > Cl_2 > Br_2 > I_2$

Colour and physical state : F_2 (pale yellow gas), Cl_2 (greenish yellow gas), Br_2 (reddish brown liquid), I_2 (purple solid).

Bond energy : $Cl_2 > Br_2 > F_2 > I_2$

Atomic radii : Increase down the group.

Melting and boiling points : Increase down the group.

Ionisation enthalpy : Very high and decreases down the group.

Electron gain enthalpy : Cl > F > Br > I

Electronegativity : Decreases down the group.

Chemical Properties

Chemical properties

Oxidation state

F shows only – 1 oxidation state (except +1 in HOF while other elements show –1, +1, +3, +5 and +7 oxidation states also.

Hydrogen halides

Boiling points : HF > HI > HBr > HCl
Melting points : HI > HF > HBr > HCl
Bond lengths : HI > HBr > HCl > HF
Bond dissociation enthalpy : HF > HCl > HBr > HI
Acidic strength : HI > HBr > HCl > HF
Thermal stability : HF > HCl > HBr > HI
Reducing power : HI > HBr > HCl > HF

Oxides

OF_2, O_2F_2
Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7
Br_2O, BrO_2, BrO_3
I_2O_4, I_4O_9
All are covalent and powerful oxidising agents.
Oxidising power : $Cl_2O > ClO_2 > Cl_2O_6 > Cl_2O_7$
Stability : $Cl_2O < ClO_2 < Cl_2O_6 < Cl_2O_7$

Oxoacids

Acid strength : $HClO_4 > HClO_3 > HClO_2 > HClO$; $HOCl > HOBr > HOI$
Oxidising power : $HOCl \simeq HOBr > HOI$;
$BrO_4^- > IO_4^- > ClO_4^-$
$HClO_4 < HClO_3 < HClO_2 < HClO$

Important Compounds of Halogen Family

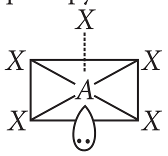
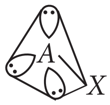
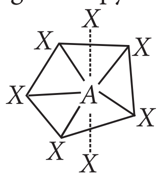
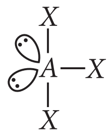
Compounds	Preparation	Properties
Chlorine (Cl_2)	**Laboratory method :** $2NaCl + 3H_2SO_4 + MnO_2 \longrightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2$	$Cl_2 + 2FeSO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + HCl$ $Cl_2 + H_2S \longrightarrow 2HCl + S$ $Cl_2 + 2NaOH_{(dil.)} \longrightarrow NaCl + NaOCl + H_2O$ $3Cl_2 + 6NaOH_{(conc.)} \longrightarrow 5NaCl + NaClO_3 + 3H_2O$ $Cl_2 \xrightarrow{H_2O} 2HCl + [O] \xrightarrow[\text{substance}]{\text{Coloured}} \text{Colourless}$
Hydrogen Chloride (HCl)	$NaCl + H_2SO_4 \xrightarrow{420\ K} NaHSO_4 + HCl$ $NaHSO_4 + NaCl \xrightarrow{823\ K} Na_2SO_4 + HCl$	Colourless and pungent smelling gas, easily liquifiable, extremely soluble in water. $Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$ $Na_2SO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2$

Oxoacids of halogens :

Oxidation state of halogen	Chlorine	Bromine	Iodine	Name of acid
+1	HClO	HBrO	HIO	Hypohalous
+3	$HClO_2$	–	–	Halous
+5	$HClO_3$	$HBrO_3$	HIO_3	Halic
+7	$HClO_4$	$HBrO_4$	HIO_4 H_5IO_6	Perhalic

Interhalogen Compounds

Properties					
Covalent in nature	Strong oxidising agents	Diamagnetic in nature	Reactive than halogens	Partially ionised in solution or in liquid state	Coloured in nature

Types of interhalogen compounds			
AX_5 sp^3d^2 Square pyramidal 	AX sp^3 Linear 	AX_7 sp^3d^3 Pentagonal bipyramidal 	AX_3 sp^3d T-shaped 

GROUP 18 ELEMENTS (NOBLE OR INERT GASES)

- **Electronic configuration : He(2)** - $1s^2$; **Ne(10)** - $[He]2s^22p^6$; **Ar(18)** - $[Ne]3s^23p^6$; **Kr(36)** - $[Ar]3d^{10}4s^24p^6$; **Xe(54)** - $[Kr]4d^{10}5s^25p^6$; **Rn(86)** - $[Xe]4f^{14}5d^{10}6s^26p^6$

Physical Properties

Group 18 Elements ($ns^2\ np^6$)

Physical state : All are monoatomic gases.

Ease of liquefication : Increases down the group.

Atomic radii : Increase down the group.

Ionisation enthalpy : Decreases down the group.

Electron gain enthalpy : Positive

Melting and boiling points : Very low due to weak dispersion forces.

Compounds of Xenon

Compound	Preparation	Properties
Xenon difluoride (XeF_2)	$Xe + F_2 \xrightarrow{\text{673 K, 1 bar}} XeF_2$ (Xe in excess)	Linear, sp^3d
Xenon tetrafluoride (XeF_4)	$Xe + 2F_2 \xrightarrow[\text{6-7 bar}]{\text{873 K}} XeF_4$ (1 : 5)	Square planar, dsp^2
Xenon hexafluoride (XeF_6)	$Xe + 3F_2 \xrightarrow[\text{60-70 bar}]{\text{573 K}} XeF_6$ (1 : 20)	Distorted octahedral, sp^3d^3
Xenon trioxide (XeO_3)	$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$	Pyramidal, sp^3
Xenon oxydifluoride ($XeOF_2$)	$XeF_4 + H_2O \longrightarrow XeOF_2 + 2HF$	T-shaped, sp^3d
Xenon oxytetrafluoride ($XeOF_4$)	$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$	Square pyramidal, sp^3d^2
Xenon dioxydifluoride (XeO_2F_2)	$XeOF_4 + H_2O \longrightarrow XeO_2F_2 + 2HF$	Distorted trigonal bipyramidal, sp^3d

INFO SHOTS

Helium in daily life !

Helium is the second most abundant element in the universe and was discovered on the sun before it was found on the earth. It is an important component in both the proton-proton reaction and the carbon cycle, which account for the energy of the sun and stars. It is commercially recovered from natural gas deposits. Liquid helium's use in magnetic resonance imaging (MRI) continues to increase because of its low boiling point which makes it useful for cooling metals needed for superconductivity, from cooling the superconducting magnets in medical MRI scanners to maintain the low temperature of the Large Hadron Collider at Cern.

SPEED PRACTICE

1. The ease of hydrolysis of trichlorides of group 15 elements decreases in the order
   (a) $NCl_3 > PCl_3 > AsCl_3 > SbCl_3 > BiCl_3$
   (b) $PCl_3 > NCl_3 > AsCl_3 > SbCl_3 > BiCl_3$
   (c) $AsCl_3 > NCl_3 > PCl_3 > SbCl_3 > BiCl_3$
   (d) $SbCl_3 > BiCl_3 > PCl_3 > NCl_3 > AsCl_3$

2. Among the following statements which one is incorrect?
   (a) Nitrogen has the ability to form $p\pi$-$p\pi$ bonds with itself.
   (b) Bismuth forms metallic bonds in elemental state.
   (c) Catenation tendency is higher in nitrogen when compared with other elements of the same group.
   (d) Nitrogen has higher first ionization enthalpy when compared with other elements of the same group.

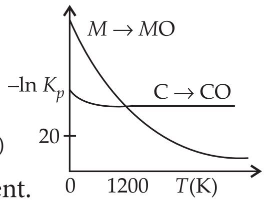
3. Bauxite ore is made up of Al_2O_3, SiO_2, TiO_2 and Fe_2O_3. This ore is treated with conc. NaOH solution at 500 K and 35 bar pressure for few hours and filtered hot. In the filtrate, the species present is/are
   (a) $Na[Al(OH)_4]$ only (b) $Na_2[Ti(OH)_6]$ only
   (c) both $Na[Al(OH)_4]$ and Na_2SiO_3
   (d) Na_2SiO_3 only.

4. In a mixture of PbS, ZnS and FeS_2, each component is separated from other in froth floatation process by using the reagents
   (a) potassium ethyl xanthate, KCN
   (b) potassium ethyl xanthate, KCN, NaOH, copper sulphate, acid
   (c) KCN, $CuSO_4$, acid (d) none of these.

5. The pair in which phosphorus atoms have a formal oxidation state of + 3 is
   (a) orthophosphorous and pyrophosphorous acids
   (b) pyrophosphorous and hypophosphoric acids
   (c) orthophosphorous and hypophosphoric acids
   (d) pyrophosphorous and pyrophosphoric acids.
   (JEE Main 2016)

6. Identify the correct sequence of increasing number of π-bonds in structures of the following molecules.
   (I) $H_2S_2O_6$ (II) H_2SO_3 (III) $H_2S_2O_5$
   (a) I, II, III (b) II, III, I
   (c) II, I, III (d) I, III, II

7. The plot shows the variation of $-\ln K_p$ versus temperature for the two reactions :
   $$M_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow MO_{(s)}$$
   and $$C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$$



   Identify the correct statement.
   (a) At $T < 1200$ K, oxidation of carbon is unfavourable.
   (b) Oxidation of carbon is favourable at all temperatures.
   (c) At $T < 1200$ K, the reaction $MO_{(s)} + C_{(s)} \rightarrow M_{(s)} + CO_{(g)}$ is spontaneous.
   (d) At $T > 1200$ K, carbon will reduce $MO_{(s)}$ to $M_{(s)}$.
   (JEE Main 2016)

8. In qualitative analysis when H_2S is passed through an aqueous solution of salt acidified with dil. HCl, a black precipitate is obtained. On boiling the precipitate with dil. HNO_3, it forms a solution of blue colour. Addition of excess of aqueous solution of ammonia to this solution gives
(a) deep blue precipitate of $Cu(OH)_2$
(b) deep blue solution of $[Cu(NH_3)_4]^{2+}$
(c) deep blue solution of $Cu(NO_3)_2$
(d) deep blue solution of $Cu(OH)_2 \cdot Cu(NO_3)_2$.

9. Identify the incorrect statement.
(a) The S—S—S bond angles in the S_8 and S_6 rings are the same.
(b) Rhombic and monoclinic sulphur have S_8 molecules.
(c) S_2 is paramagnetic like oxygen.
(d) S_8 ring has a crown shape. **(JEE Main 2016)**

10. 'Lapis-Lazuli' is a blue coloured precious stone. It is mineral of the class
(a) sodium alumino silicate
(b) basic copper carbonate
(c) zinc cobalt (d) prussian blue.

11. Which of the following involves both calcination and carbon reduction processes to obtain metal from its ore?
(a) Zinc from zinc carbonate
(b) Calcium from calcium carbonate
(c) Copper from copper sulphide.
(d) None of these.

12. The correct statement regarding, (i) HClO, (ii) $HClO_2$, (iii) $HClO_3$ and (iv) $HClO_4$, is/are
(a) the number of Cl=O bonds in (ii) and (iii) together is two
(b) the number of lone pairs of electrons on Cl in (ii) and (iii) together is three
(c) the hybridization of Cl in (iv) is sp^2
(d) amongst (i) to (iv), the strongest acid is (i).

13. "Metals are usually not found as nitrates in their ores." Out of the following two (I and II) reasons which is/are true for the above observation?
I. Metal nitrates are highly unstable.
II. Metal nitrates are highly soluble in water.
(a) I is false but II is true.
(b) I is true but II is false.
(c) I and II are true.
(d) I and II are false. **(AIPMT 2015)**

14. Compounds *A* and *B* are treated with dil. HCl separately. Compound *A* gives a gas *X* having pungent smell of burning sulphur and the solution is turned turbid while the compound *B* gives a gas *Y* having a smell of rotten eggs. The gases *X* and *Y* react with each other giving same product as was formed in the turbid solution of *A*. The compounds *A* and *B* are respectively
(a) $Na_2S_2O_3$, Na_2S (b) $Na_2S_2O_3$, Na_2SO_4
(c) Na_2S, Na_2SO_3 (d) Na_2SO_3, Na_2SO_4

15. In analogy to $O_2^+[PtF_6]^-$ a compound $N_2^+[PtF_6]^-$ will not be formed because
(a) the ionisation enthalpy of N_2 gas is higher than that of O_2 gas
(b) the ionisation enthalpy of N_2 gas is lower than that of O_2 gas
(c) the ionisation enthalpy of N_2 gas is higher than that of N atom
(d) none of these.

16. Which of the following statements is correct regarding the slag obtained during the extraction of a metal like copper or iron?
(a) The slag is lighter and has higher melting point than the metal.
(b) The slag is lighter and has lower melting point than the metal.
(c) The slag is heavier and has higher melting point than the metal.
(d) The slag is heavier and has lower melting point than the metal.

17. Match items of Column I with the items of Column II and assign the correct code :

	Column I		Column II
(A)	Cyanide process	(i)	Ultrapure Ge
(B)	Froth floatation process	(ii)	Dressing of ZnS
(C)	Electrolytic reduction	(iii)	Extraction of Al
(D)	Zone refining	(iv)	Extraction of Au
		(v)	Purification of Ni

	A	B	C	D
(a)	(i)	(ii)	(iii)	(iv)
(b)	(iii)	(iv)	(v)	(i)
(c)	(iv)	(ii)	(iii)	(i)
(d)	(ii)	(iii)	(i)	(v)

(NEET 2016)

18. When copper pyrites is roasted in excess of air, a mixture of CuO and FeO is formed. FeO is present as impurities. This can be removed as slag during reduction of CuO. The flux added to form slag is
(a) SiO_2, which is an acidic flux
(b) lime stone, which is a basic flux
(c) SiO_2, which is a basic flux
(d) CaO, which is a basic flux.

19. Which statement is correct about the oxyacids of phosphorus?
(a) Basicity of both H_3PO_4 and H_3PO_3 is 3.
(b) Acidity of both H_3PO_4 and H_3PO_3 is 3.
(c) Acidity of H_3PO_4 and H_3PO_3 is 3 and 2 respectively.
(d) Basicity of H_3PO_4 and H_3PO_3 is 3 and 2 respectively.

20. A metal, *M* forms chlorides in its +2 and +4 oxidation states. Which of the following statements about these chlorides is correct?
(a) MCl_2 is more volatile than MCl_4.
(b) MCl_2 is more soluble in anhydrous ethanol than MCl_4.
(c) MCl_2 is more ionic than MCl_4.
(d) MCl_2 is more easily hydrolysed than MCl_4.

21. Sulphide ores of metals are usually concentrated by froth floatation process. Which one of the following sulphide ores offer an exception and is concentrated by chemical leaching?
(a) Galena (b) Copper pyrite
(c) Sphalerite (d) Argentite

22. The method of zone refining of metals is based on the principle of
(a) greater mobility of the pure metal than that of the impurity.
(b) higher melting point of the impurity than that of the pure metal.
(c) greater noble character of the solid metal than that of the impurity.
(d) greater solubility of the impurity in the molten state than in the solid.

23. Acidity of diprotic acids in aqueous solution increases in the order
(a) $H_2S < H_2Se < H_2Te$ (b) $H_2Se < H_2S < H_2Te$
(c) $H_2Te < H_2S < H_2Se$ (d) $H_2Se < H_2Te < H_2S$
(AIPMT 2014)

24. The temperature of blast furnace to produce iron from its ore Fe_2O_3 varies from 500°C at the top of the furnace to about 1900°C at the bottom of the furnace. The reaction between the ore Fe_2O_3 and CO at the lowest temperature (~ 500°C) is
(a) $3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$
(b) $Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$
(c) $Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$
(d) $Fe_2O_3 + CO + CaCO_3 \longrightarrow Fe_2O_3 + CO + CO_2 + CaO$

25. 'Sulphan' is
(a) a mixture of SO_3 and H_2SO_5
(b) 100% conc. H_2SO_4
(c) a mixture of gypsum and conc. H_2SO_4
(d) 100% oleum (a mixture of 100% SO_3 and 100% H_2SO_4).

26. Which of the following factors is of no significance for roasting sulphide ores to the oxides and not subjecting the sulphide ores to carbon reduction directly?
(a) CO_2 is more volatile than CS_2.
(b) Metal sulphides are thermodynamically more stable than CS_2.
(c) CO_2 is thermodynamically more stable than CS_2.
(d) Metal sulphides are less stable than the corresponding oxides.

27. A dark brown solid (*X*) reacts with NH_3 to form a mild explosive which decomposes to give a violet coloured gas. (*X*) also reacts with H_2 to give an acid (*Y*). (*Y*) can also be prepared by heating its salt with H_3PO_4. *X* and *Y* are respectively
(a) Cl_2, HCl (b) SO_2, H_2SO_4
(c) Br_2, HBr (d) I_2, HI

28. Oxidation states of the metal in the minerals haematite and magnetite, respectively are
(a) II, III in haematite and III in magnetite
(b) II, III in haematite and II in magnetite
(c) II in haematite and II, III in magnetite
(d) III in haematite and II, III in magnetite.

29. On reaction with Cl_2, phosphorus forms two types of halides '*A*' and '*B*'. Halide '*A*' is yellowish white powder but halide '*B*' is colourless oily liquid. Which of the following are their hydrolysis products respectively?
(I) H_3PO_2 (III) H_3PO_3
(II) H_3PO_4 (IV) H_3PO_5
(a) I and II (b) II and III
(c) III and IV (d) I and IV

30. In Serpek's process, byproduct obtained in the purification of bauxite is
(a) Al_2O_3 (b) N_2
(c) NH_3 (d) none of these.

SOLUTIONS

1. **(a) :** As the electronegativity of the central metal atom M in MCl_3 decreases down the group in nitrogen family, the tendency to attract lone pair of electrons from water molecule decreases. Hence, the ease of hydrolysis decreases from top to bottom.

2. **(c) :** Catenation tendency is higher in phosphorus when compared with other elements of the same group.

3. **(c) :** $Al_2O_3 \cdot 2H_2O + 2NaOH + H_2O \xrightarrow[35\text{ bar}]{500\text{ K}} 2Na[Al(OH)_4]$

$SiO_2 + 2NaOH \xrightarrow[35\text{ bar}]{500\text{ K}} \underset{\text{Sodium silicate}}{Na_2SiO_3} + H_2O$

4. **(b) :** Potassium ethyl xanthate acts as a collector. KCN and NaOH depress the floatation property of ZnS and FeS_2 particles. Thus, only PbS particles go into the froth. Now copper sulphate is added to the tank (mixture) which activates floating character of ZnS and this time only ZnS comes along with froth. The remaining slurry is acidified and FeS_2 floats along with froth.

5. **(a) :**

Name	Formula	Oxidation state
Orthophosphorous acid	H_3PO_3	+3
Pyrophosphorous acid	$H_4P_2O_5$	+3
Hypophosphoric acid	$H_4P_2O_6$	+4
Pyrophosphoric acid	$H_4P_2O_7$	+5

6. **(b) :** $H_2S_2O_6$, $HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$: 4 π-bonds ;

H_2SO_3, $HO-\overset{\overset{O}{\|}}{S}-OH$: one π-bond ;

$H_2S_2O_5$, $HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\underset{\underset{O}{\|}}{S}-OH$: 3 π-bonds.

7. **(c) :** In the given Ellingham diagram, below 1200 K the C $\rightarrow$ CO curve lies below the $M \rightarrow MO$ curve hence, carbon can reduce MO.

8. **(b) :** In qualitative analysis, when H_2S is passed through an aqueous solution of salt acidified with dil. HCl, a black ppt. of CuS is obtained.

$CuSO_4 + H_2S \xrightarrow{\text{dil. HCl}} \underset{\text{Black ppt.}}{CuS} + H_2SO_4$

On boiling CuS with dil. HNO_3 it forms a blue coloured solution and the following reactions occur :

$3CuS + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 3S + 4H_2O$

$S + 2HNO_3 \longrightarrow H_2SO_4 + NO$

$2Cu^{2+} + SO_4^{2-} + 2NH_3 + 2H_2O \longrightarrow Cu(OH)_2 \cdot CuSO_4 + 2NH_4OH$

$Cu(OH)_2 \cdot CuSO_4 + 8NH_3 \longrightarrow \underset{\substack{\text{Tetraamminecopper (II)}\\ \text{(Deep blue solution)}}}{2[Cu(NH_3)_4]^{2+}} + 2OH^- + SO_4^{2-}$

9. **(a) :** Sulphur having puckered S_8 rings has crown conformation and Engel's sulphur contains S_6 rings arranged in a chair conformation.

10. **(a) :** 'Lapis–Lazuli' is the sodium aluminosilicate, present in earth rocks as blue stone.

11. **(a) :** $\longrightarrow$

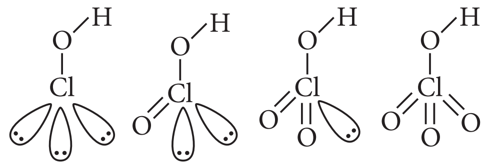
$\longrightarrow$

$\xrightarrow{\Delta}$

$\longrightarrow$

$- \longrightarrow$

$\longrightarrow$ 2

12. **(b) :** 

Hypochlorous acid (HClO)	Chlorous acid ($HClO_2$)	Chloric acid ($HClO_3$)	Perchloric acid ($HClO_4$)

In all these oxoacids, Cl is sp^3-hybridized.

Acid strength of oxoacids of the same halogen decreases with decrease in oxidation number of the halogen, *e.g.*,

$\overset{+7}{HClO_4} > \overset{+5}{HClO_3} > \overset{+3}{HClO_2} > \overset{+1}{HClO}$

13. **(a) :** All nitrates are soluble in water and are quite stable as they do not decompose easily on heating.

14. **(a) :** The gas X having smell of burning sulphur is SO_2 and the compound A is $Na_2S_2O_3$ which gives a turbid solution due to formation of colloidal sulphur on reacting with dil. HCl.

$\underset{A}{Na_2S_2O_3} + 2HCl_{(dil.)} \longrightarrow 2NaCl + H_2O + \underset{X}{SO_2} + \underset{\text{Colloidal sulphur}}{S}$

The gas Y having smell of rotten eggs is H_2S and the compound B is Na_2S.

$\underset{B}{Na_2S} + 2HCl \longrightarrow 2NaCl + \underset{Y}{H_2S}$

$\underset{X}{SO_2} + \underset{Y}{2H_2S} \longrightarrow 2H_2O + \underset{\text{Colloidal sulphur}}{3S}$

15. (a) : Ionisation enthalpy of N_2 gas (1503 kJ mol^{-1}) is higher than that of O_2 gas (1175 kJ mol^{-1}) and it cannot lose its electron so easily as O_2 does in forming $O_2^+[PtF_6]^-$ compound.

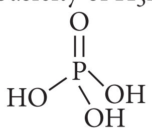
16. (b) : Slag is lighter, has lower melting point than metal, floats and can be skimmed off.

17. (c) : Mac-Arthur Forest cyanide process is used for the extraction of gold and silver.
Froth floatation process is used for the concentration of sulphide ores *e.g.*, ZnS.
Electrolytic reduction is used for the extraction of highly electropositive metals like Na, K, Mg, Ca, Al, etc.
Zone refining method is used for producing semiconductor and other metals of very high purity *e.g.*, Ge, Si, B, Ga and In. Purification of Ni is done by vapour phase refining (Mond's process).

18. (a) : FeO (being basic) combines with silica (SiO_2) an acidic flux to give $FeSiO_3$ slag.

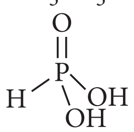
$$FeO + SiO_2 \longrightarrow FeSiO_3 \text{ (slag)}$$

19. (d) : Orthophosphoric acid (H_3PO_4) is a tribasic acid because it has three replaceable hydrogen atoms. Hence, the basicity of H_3PO_4 is 3.



H_3PO_4 (tribasic acid)

While phosphorous acid (H_3PO_3) is a dibasic acid because it has two replaceable hydrogen atoms. Hence, the basicity of H_3PO_3 is 2.



H_3PO_3 (dibasic acid)

20. (c) : MCl$_2$: Oxidation state of $M = +2$
MCl$_4$: Oxidation state of $M = +4$
Higher the oxidation state, smaller the size, greater the polarizing power, greater the covalent character. Hence, MCl$_4$ is more covalent and MCl$_2$ is more ionic.

21. (d) : Leaching process involves the treatment of the ore with a suitable reagent as to make it soluble while impurities remain insoluble. The ore is recovered from the solution by suitable chemical method. Argentite or silver glance, Ag_2S is an ore of silver. Silver is extracted from argentite by the Mac-Arthur and Forest process (leaching process).

$$Ag_2S + 4NaCN \rightleftharpoons 2Na[Ag(CN)_2] + Na_2S$$
$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag$$

22. (d) : Elements which are used as semiconductors such as Si, Ge, Ga, etc. are refined by this method, which is based on the difference in solubility of impurities in molten and solid state of the metal.

23. (a) : As the atomic size increases down the group, the bond length increases and the bond strength decreases and the cleavage of M—H bond becomes easier thus, more will be the acidity. Hence, the correct order is : $H_2S < H_2Se < H_2Te$.

24. (c) : At the top of the blast furnace (lowest temperature ~ 500°C) the reaction is

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

25. (d)

26. (a) : Oxidising roasting is a very common type of roasting in metallurgy and is carried out to remove sulphur and arsenic in the form of their volatile oxides. CS_2 is more volatile than CO_2. So, option (a) is of no significance for roasting sulphide ores to their oxides. The reduction process is on the thermodynamic stability of the products and not on their volatility.

27. (d) : $X = I_2$, $Y = HI$

$$\underset{(X)}{3I_2} + 2NH_3 \longrightarrow \underset{\text{(Explosive)}}{NH_3{\cdot}NI_3}$$
$$8NI_3{\cdot}NH_3 \longrightarrow 5N_2 + 9I_2 + 6NH_4I$$
$$\underset{(X)}{I_2} + H_2 \longrightarrow \underset{(Y)}{2HI}$$
$$3NaI + H_3PO_4 \xrightarrow{\Delta} Na_3PO_4 + \underset{(Y)}{3HI}$$

28. (d) : Haematite – Fe_2O_3
O.S. of Fe = +3
Magnetite – $Fe_3O_4(FeO + Fe_2O_3)$
O.S. of Fe = +2, +3

29. (b) : 'A' is PCl_5 and 'B' is PCl_3.

$$P_4 + 10Cl_2 \longrightarrow 4PCl_5$$
$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

When 'A' and 'B' are hydrolysed

$$\underset{\substack{(A)\\ \text{Phosphorus}\\ \text{pentachloride}}}{PCl_5} + 4H_2O \longrightarrow \underset{\substack{\text{Phosphoric}\\ \text{acid}}}{H_3PO_4} + 5HCl$$
$$\underset{\substack{(B)\\ \text{Phosphorus}\\ \text{trichloride}}}{PCl_3} + 3H_2O \longrightarrow \underset{\substack{\text{Phosphorous}\\ \text{acid}}}{H_3PO_3} + 3HCl$$

30. (c) : $SiO_2 + 2C \longrightarrow Si + 2CO\uparrow$

$$Al_2O_3{\cdot}2H_2O + 3C + N_2 \longrightarrow 2AlN + 3CO + 2H_2O$$
$$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$$

◆◆

EXAMINER'S MIND CLASS XII

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XII.
This year JEE (Main & Advanced)/NEET/AIIMS have drawn their papers heavily from NCERT books.

Section - I	Q. 1 to 10 Only One Option Correct Type MCQs.
Section - II	Q. 11 to 13 More than One Options Correct Type MCQs.
Section - III	Q. 14 to 17 Paragraph Type MCQs having Only One Option Correct.
Section - IV	Q. 18 & 19 Matching List Type MCQs having Only One Option Correct.
Section - V	Q. 20 to 22 Assertion Reason Type MCQs having Only One Option Correct. Mark the correct choice as : (a) If both assertion and reason are true and reason is the correct explanation of assertion. (b) If both assertion and reason are true but reason is not the correct explanation of assertion. (c) If assertion is true but reason is false. (d) If both assertion and reason are false.
Section - VI	Q. 23 to 25 Integer Value Correct Type Questions having Single Digit Integer Answer, ranging from 0 to 9 (both inclusive).

The *p*-BLOCK ELEMENTS (GROUP 15 TO 18)

SECTION - I

Only One Option Correct Type

1. Copper metal on treatment with dilute HNO_3 produces a gas (X). (X) when combines with (Y), an iron containing brown complex (Z) is obtained. Complex (Z) is
   (a) $[Fe(H_2O)_5NO]^+$ (b) $[Fe(H_2O)_5NO]^{2+}$
   (c) $[Fe(H_2O)_5NO_2]^+$ (d) $[Fe(H_2O)_5NO_2]^{2+}$

2. Chlorine cannot displace
   (a) iodine from NaI (b) bromine from NaBr
   (c) fluorine from NaF (d) none of these.

3. Which among the following is a tetrabasic acid?
   (a) Orthophosphorous acid
   (b) Orthophosphoric acid
   (c) Metaphosphoric acid
   (d) Pyrophosphoric acid

4. An oxide of a non-metal has the following properties :
   (i) It acts both as a proton donor as well as proton acceptor.
   (ii) It reacts readily with basic and acidic oxides.
   (iii) It oxidises Fe at its boiling point.
   The oxide is
   (a) P_2O_5 (b) SiO_2 (c) H_2O (d) CO_2

5. Which one is not an acid?
   (a) NaH_2PO_2 (b) NaH_2PO_3
   (c) NaH_2PO_4 (d) None of these

6. Which of the following statements is incorrect?
   (a) ONCl and ONO^- are isoelectronic.
   (b) O_3 molecule is bent.
   (c) Ozone is violet-black in solid state.
   (d) Ozone is diamagnetic gas.

7. The stability of interhalogen compounds follows the order :
   (a) $IF_3 > BrF_3 > ClF_3$ (b) $BrF_3 > IF_3 > ClF_3$
   (c) $ClF_3 > BrF_3 > IF_3$ (d) $ClF_3 > IF_3 > BrF_3$

8. Which of the following statements is correct?
   (a) Helium has the lowest melting point and boiling point.
   (b) Helium can diffuse through rubber, PVC and even glass.
   (c) Ar, Kr and Xe form clathrate compounds.
   (d) All the above statements are correct.

9. Among the following molecules :
(i) XeO_3 (ii) $XeOF_4$ (iii) XeF_6
those having same number of lone pairs on Xe are
(a) (i) and (ii) only (b) (i) and (iii) only
(c) (ii) and (iii) only (d) all of these.

10. Which one of the following statements is incorrect?
(a) pK_a value of HI (strongest halogen acid) is most positive.
(b) High H—F bond strength makes H—F a weak acid in dilute aqueous solution.
(c) Helium and Neon do not form clathrates.
(d) K_a values of HX is in order HF < HCl < HBr < HI.

SECTION - II

More than One Options Correct Type

11. Concentrated sulphuric acid is
(a) oxidising agent (b) hygroscopic
(c) efflorescent (d) sulphonating agent.

12. Which of the following statements are true?
(a) Sulphur exhibits 6 coordination number in its compound.
(b) Bond energy of F_2 is less than Cl_2.
(c) PCl_5 does not exist but NCl_5 exists.
(d) Elements of 15^{th} group show only + 3 and +5 oxidation states.

13. White phosphorus (P_4) has
(a) six P—P single bonds
(b) four P—P single bonds
(c) four lone pairs of electrons
(d) PPP angle of 60°.

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

Due to the presence of two lone pairs of electrons on the central atom, hydrides of group 16 elements have bent or V-Shape. The central atom in these hydrides is sp^3 hybridised. Due to strong H-bonding melting and boiling points of hydrides of oxygen are very high. On moving down the group, the covalent character increases. This can be explained on the basis of Fajan's rule, which states that the tendency to form covalent bonds increases as the size of the anion M^{2-} increases. As the size of the atom in H_2M increases, the strength of H—M bond decreases. Hence, the tendency to release hydrogen as proton increases down the group.

14. Bond angle is minimum for
(a) H_2Se (b) H_2S (c) H_2Te (d) H_2O

15. Which one of the following hydrides is most acidic?
(a) H_2S (b) H_2Te (c) H_2O (d) H_2Se

Paragraph for Questions 16 and 17

The pronounced change from non-metallic behaviour and the increase in basicity of oxides from N, P, As, Sb to Bi is principally due to the increasing size of the atoms. The ionisation potential values indicate that it is much more difficult to pull electrons of small nitrogen atom than the larger bismuth atom. It is interesting to note that nitrogen obtained from the decomposition of compounds such as NH_4NO_2 is of lower density than the residual gas obtained from the atmosphere by removal of oxygen, carbon dioxide and water.

16. Which of the following oxides is most acidic?
(a) As_2O_3 (b) Bi_2O_3 (c) Sb_2O_3 (d) P_2O_3

17. Which of the following hydrides would be most basic?
(a) PH_3 (b) AsH_3 (c) NH_3 (d) SbH_3

SECTION - IV

Matching List Type

18. Match the List I with the List II and select the correct answer using the codes given below the lists :

	List I (Mixtures)		List II (Reagents used for separation)
P.	N_2 and CO	1.	Water
Q.	N_2 and O_2	2.	H_2SO_4
R.	N_2 and NH_3	3.	Ammonical cuprous chloride
S.	PH_3 and NH_3	4.	Pyrogallol

	P	Q	R	S
(a)	1	2	3	4
(b)	4	3	2	1
(c)	3	4	2	1
(d)	3	4	1	2

19. Match the following unbalanced reactions of List I with the respective missing reagents or conditions listed in List II and select the correct answer using the codes given below the lists :

	List I		List II
P.	$PbO_2 + H_2SO_4 \rightarrow PbSO_4 + O_2$ + by products	1.	NO
Q.	$Na_2S_2O_3 + H_2O \rightarrow NaHSO_4$ + by products	2.	I_2
R.	$N_2H_4 \rightarrow N_2$ + by products	3.	Warm
S.	$XeF_2 \rightarrow Xe$ + by products	4.	Cl_2

	P	Q	R	S
(a)	3	4	2	1
(b)	1	4	3	2
(c)	4	3	2	1
(d)	3	4	1	2

SECTION - V

Assertion Reason Type

20. **Assertion :** The aqueous solution of XeF_2 is a powerful oxidising agent.
Reason : Hydrolysis of XeF_2 is slow in dilute acid but rapid in basic solution.

21. **Assertion :** F atom has a less negative electron affinity than Cl atom.
Reason : Additional electrons are repelled more effectively by $3p$ electrons in Cl atom than by $2p$ electrons in F atom.

22. **Assertion :** Chlorine and sulphur dioxide both are bleaching agents.
Reason : The bleaching action of chlorine and sulphur dioxide is performed through the process of oxidation.

SECTION - VI

Integer Value Correct Type

23. Total number of oxides which are colourless in the given list of oxides is
$NO, N_2O, N_2O_3, N_2O_4, N_2O_5$

24. Oxyacids of sulphur are listed below. The number of oxyacids in which sulphur is present in +6 oxidation state is
$H_2SO_3, H_2SO_4, H_2S_2O_4, H_2S_2O_7, H_2S_2O_6, H_2SO_5, H_2S_2O_8$

25. The number of P—O—P bonds in P_4O_{10} is

ALCOHOLS, PHENOLS AND ETHERS

SECTION - I

Only One Option Correct Type

1. Consider the following reactions :

I. $CH_3CH_2\underset{OH}{CH}CH_3 \xrightarrow{H^+} A$(major)

II. $CH_3\underset{CH_3}{\overset{CH_3}{C}}-\underset{OH}{CH}CH_3 \xrightarrow{H^+} B$(major)

A and *B* are respectively

(a) $CH_3CH{=}CHCH_3$, $CH_3\underset{CH_3}{\overset{CH_3}{C}}CH{=}CH_2$

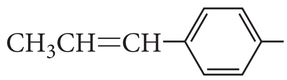
(b) $CH_3CH_2CH{=}CH_2$, $CH_3\underset{CH_3}{\overset{CH_3}{C}}CH{=}CH_2$

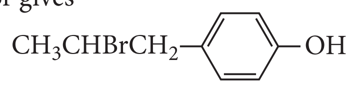
(c) $CH_3CH{=}CHCH_3$, $CH_3\underset{CH_3}{C}{=}\underset{CH_3}{C}CH_3$

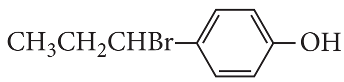
(d) $CH_3CH_2CH{=}CH_2$, $CH_3\underset{CH_3}{C}{=}\underset{CH_3}{C}CH_3$

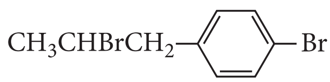
2. Products $(P_2) \xleftarrow{\text{anhy. HI}} (CH_3)_3C—O—CH_3 \xrightarrow{\text{conc. HI}}$ Products(P_1)

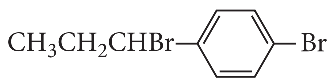
The products P_1 and P_2 respectively are
(a) $(CH_3)_3COH + CH_3I$ and $(CH_3)_3CI + CH_3OH$
(b) $(CH_3)_3CI + CH_3OH$ and $(CH_3)_3COH + CH_3I$
(c) $(CH_3)_3CI + CH_3OH$ in both cases
(d) CH_3I and $(CH_3)_3COH$ in both cases.

3. The reaction of  with HBr gives

(a) 

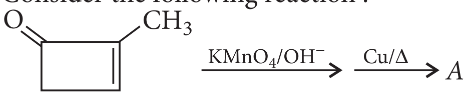
(b) 

(c) 

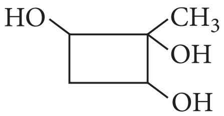
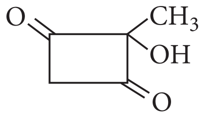
(d) 

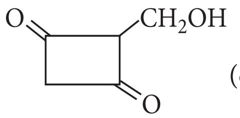
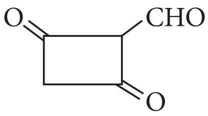
4. An organic compound of molecular formula $C_4H_{10}O$ does not react with sodium. With excess of HI, it gives only one type of alkyl halide. The compound is
(a) ethoxyethane (b) 2-methoxypropane
(c) 1-methoxypropane (d) 1-butanol.

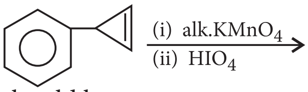
5. Consider the following reaction :

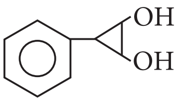
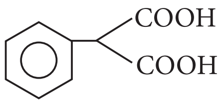


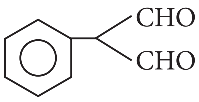
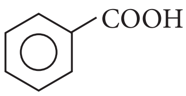
A formed is

(a)  (b) 

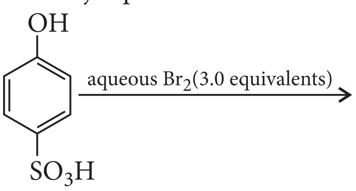
(c)  (d) 

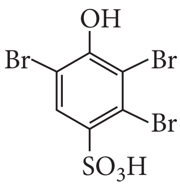
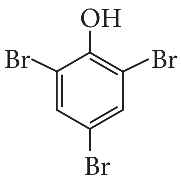
6.  P. The compound P should be

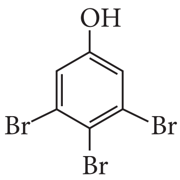
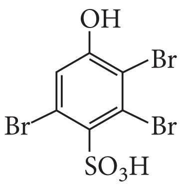
(a)  (b) 

(c)  (d) 

7. The major product of the following reaction is



(a)  (b) 

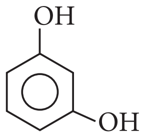
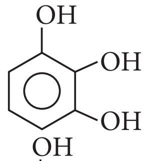
(c)  (d) 

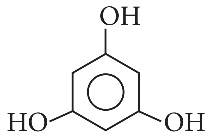
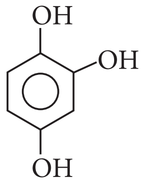
8. What is the product of the following sequence of reactions?

$(CH_3)_2C{=}CHCH_2CH_3 \xrightarrow[\text{(ii)}H_2O_2,\overline{O}H]{\text{(i) }BH_3/THF} \xrightarrow[CH_2Cl_2]{PCC} \xrightarrow[\text{(ii)}H_3O^+]{\text{(i) }CH_3MgBr}$

(a) 2, 4-Dimethyl-3-pentanol
(b) 2, 3-Dimethyl-3-pentanol
(c) 2, 3-Dimethyl-2-pentanol
(d) 2, 2-Dimethyl-3-pentanol

9. Which of the following compounds can react with hydroxylamine?

(a)  (b) 

(c)  (d) 

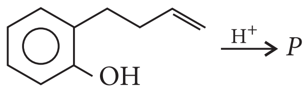
10. Ethyl alcohol cannot be used as a solvent for methyl magnesium iodide because
(a) methyl magnesium iodide reacts with alcohol giving methane.
(b) the reaction between them is explosive in nature.
(c) methyl magnesium iodide is converted to ethyl magnesium iodide.
(d) alcohol is immiscible with methyl magnesium iodide.

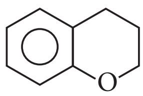
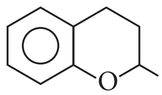
SECTION - II

More than One Options Correct Type

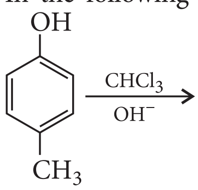
11. Which of the following compounds will give a yellow precipitate with iodine and alkali?
(a) 2-Hydroxypropane (b) Acetophenone
(c) Methyl acetate (d) Acetamide

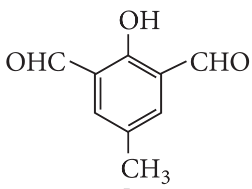
12. The correct statements about the given reaction are

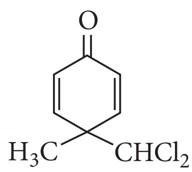


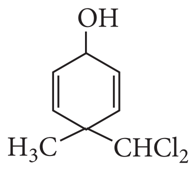
(a) protonation occurs at —OH
(b) protonation occurs at C=C bond
(c) P is  (d) P is 

13. In the following reaction, the products formed are

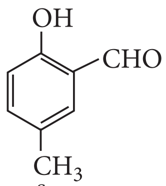



P


Q



R



S

(a) *P* (major) (b) *Q* (minor)
(c) *R* (minor) (d) *S* (major)

SECTION - III

Paragraph Type

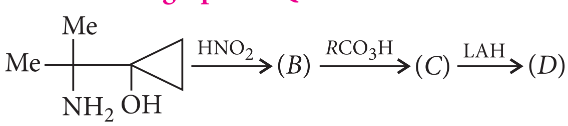
Paragraph for Questions 14 and 15

Although chlorobenzene is inert to nucleophilic substitution, it gives quantitative yield of phenol when heated with aq. NaOH at high temperature and under high pressure. Phenol so formed is a weaker acid than the carboxylic acid hence, it dissolves only in strong bases like NaOH, but not weak bases like $NaHCO_3$. It reacts with acid chlorides and acid anhydrides in the absence of $AlCl_3$ to form esters. As far as electrophilic substitution in phenol is concerned, the —OH group is an activating group, hence, its presence enhances the electrophilic substitution at *o*– and *p*-positions. Condensation with formaldehyde is one of the important property of phenol. The condensation may takes place in presence of acids or alkalis and leads to the formation of bakelite, an important industrial polymer.

14. Conversion of chlorobenzene into phenol involves
(a) modified S_N1 mechanism
(b) modified S_N2 mechanism
(c) both (a) and (b)
(d) elimination - addition mechanism.

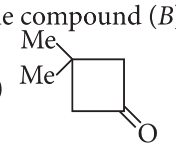
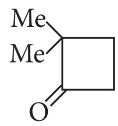
15. Phenol undergoes electrophilic substitution more readily than benzene because
(a) the intermediate carbocation is a resonance hybrid of more resonating structures than that from benzene.
(b) the intermediate is more stable as it has positive charge on oxygen, which can be better accommodated than on carbon.
(c) in one of the canonical structures, every atom (except hydrogen) has complete octet
(d) the —OH group is *o*, *p*–directing which like all other *o*, *p*-directing groups is activating.

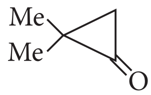
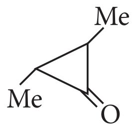
Paragraph for Questions 16 and 17



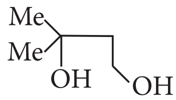
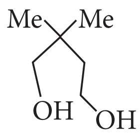
(*A*)

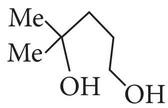
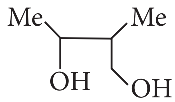
16. The compound (*B*) is

(a)  (b) 

(c)  (d) 

17. The compound (*D*) is

(a)  (b) 

(c)  (d) 

SECTION - IV

Matching List Type

18. Match the entries of List I with appropriate entries of List II and select the correct answer using the code given below the lists.

	List I		**List II**
P.	CH_3CH_2OH	1.	Reacts fastest with Lucas reagent
Q.	$CH_3CH_2CHOHCH_3$	2.	Gets easily oxidised by $K_2Cr_2O_7/H_2SO_4$
R.	C_6H_5OH	3.	Produces blue colouration in Victor-Meyer's test
S.	$(CH_3)_3COH$	4.	Produces violet colouration with neutral $FeCl_3$

	P	Q	R	S
(a)	1	2	3	4
(b)	3	2	4	1
(c)	2	3	4	1
(d)	3	1	4	2

19. Match the entries listed in List I (Boiling Points) with the entries listed in List II (Compounds) and select the correct answer using the code given below the lists :

	List I		**List II**
P.	381 K	1.	2-Methyl-2-propanol
Q.	373 K	2.	2-Butanol
R.	356 K	3.	1-Butanol
S.	390 K	4.	2-Methyl-1-propanol

	P	Q	R	S
(a)	2	3	4	1
(b)	4	3	1	2
(c)	4	2	1	3
(d)	3	2	4	1

SECTION - V

Assertion Reason Type

20. **Assertion :** High boiling point of glycerol is due to hydrogen bonding.
Reason : Glycerol decomposes much below its boiling point and evaporation is carried out in vacuum.

21. **Assertion :** Etherates are coordination complexes of ethers with Lewis acids.
Reason : Ethers are easily cleaved by mineral acids such as HCl and H_2SO_4 at 373 K.

22. **Assertion :** Boiling point of ether is smaller than that of isomeric alcohol.
Reason : Solubility of ether in water is due to H-Bonding.

SECTION - VI

Integer Value Correct Type

23. $C_2H_5-\underset{OH}{\overset{C_2H_5}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3 + C_6H_5-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-C_2H_5 \xrightarrow[\text{Heat}]{H_2SO_4}$

Number of ketones formed in the above reaction is

24. The number of ethers in the given list which cannot be prepared by Williamson's synthesis is
$CH_3OCH_2CH_3$, $C_6H_5OCH_3$, $C_6H_5OCH_2CH_3$, $(C_6H_5)_2O$, $(CH_3)_3COCH_3$, $(CH_3)_3COCH_2CH_3$, $(CH_3)_3COC(CH_3)_3$, $(C_2H_5)_2O$, $C_6H_5CH_2OC_6H_5$

25. Total number of alcohols in the given list which can be oxidized into carbonyl compounds by MnO_2/CH_2Cl_2 as an oxidising agent is
(i) $CH_3-CH=CH-CH_2-OH$
(ii) $CH_3-CH_2-CH_2-OH$
(iii) $CH_3-\underset{CH_3}{CH}-OH$
(iv) $Ph-CH_2-OH$
(v)  $-CH_2-OH$
(vi) $CH_3-C\equiv C-CH_2-OH$

SOLUTIONS

THE *p*-BLOCK ELEMENTS (GROUP 15 TO 18)

1. **(b) :** $3Cu + \underset{\text{dil.}}{8HNO_3} \longrightarrow \underset{(X)}{2NO} + 3Cu(NO_3)_2 + 4H_2O$
$\underset{(Y)}{[Fe(H_2O)_6]^{2+}} + \underset{(X)}{NO} \longrightarrow \underset{\substack{(Z)\\ \text{Brown ring complex}}}{[Fe(H_2O)_5NO]^{2+}} + H_2O$

2. **(c) :** Chlorine cannot displace fluorine from NaF because fluorine is more electronegative than chlorine.

3. **(d)**

4. **(c) :** H_2O is an amphoteric oxide. It can accept as well as donate a proton. Thus, it readily reacts with basic as well as acidic oxides. Only water vapour react with Fe.

5. **(a) :** NaH_2PO_2 is the salt of hypophosphorous acid, $H-\underset{H}{\overset{O \atop \|}{P}}-\bar{O}Na^+$. The two H-atoms in NaH_2PO_2 are not replaceable.

6. **(a)**

7. **(a) :** The stability of interhalogen compounds decreases as the size of central atom decreases due to electronegativity difference. Hence, the stability of interhalogen compounds follows the order :
$IF_3 > BrF_3 > ClF_3$

8. **(d)** **9.** **(d)** **10.** **(a)**

11. **(a, b, d) :** Concentrated sulphuric acid (H_2SO_4) is hygroscopic, oxidising agent and sulphonating agent. It is not an efflorescent compound.

12. **(a, b) :** Fluorine is more reactive than chlorine. So, bond energy of chlorine is greater than fluorine. Sulphur exhibits 6 coordination number. PCl_5 exists but NCl_5 does not exist as N cannot expand its octet due to non-availability of *d*-orbitals.
The common oxidation states of group 15 elements are –3, +3 and 5.

13. **(a,c,d)** **14.** **(c)** **15.** **(b)** **16.** **(d)**

17. **(c) :** NH_3 is distinctly basic due to the small size of the nitrogen atom. The lone pair of electrons is concentrated on a small region and hence, its electron releasing tendency is maximum.

18. **(c) :** P -(3); Q-(4); R-(2); S-(1)
CO and N_2 can be separated by bubbling through ammonical cuprous chloride in which CO is absorbed not N_2. N_2 and O_2 can be separated by bubbling through alkaline solution of pyrogallol in which oxygen is absorbed but not N_2. NH_3 and N_2

can be separated by bubbling through H_2SO_4 when NH_3 is absorbed but not N_2. Ammonia is recovered by heating the solution of $(NH_4)_2SO_4$ with excess of NaOH. PH_3 and NH_3 can be separated by bubbling through water in which NH_3 dissolves but not PH_3.

19. (a) : P–(3); Q–(4); R-(2); S-(1)

20. (b) : XeF_2 oxidises HCl to Cl_2 and Ce(III) to Ce(IV). Its oxidation potential is +2.64 V.

21. (c) **22. (c)** **23. (4)** **24. (4)** **25. (6)**

ALCOHOLS, PHENOLS AND ETHERS

1. (c)

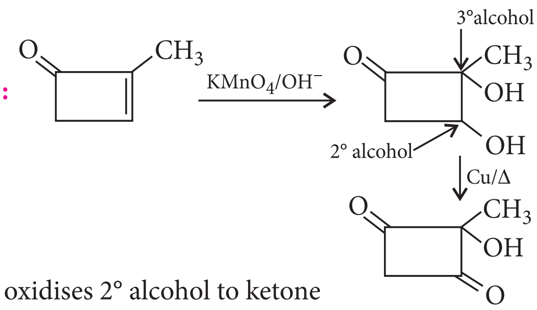
2. (b) : When one of the alkyl groups is 3° and another is 1°, nature of reagent determines the type of mechanism (S_N1 or S_N2). A polar solvent or reagent capable of forming ions (*viz.* conc. HI) will cause S_N1 reaction, while a non-polar solvent or a reagent not capable of forming ions (*viz.* anhy. HI) will cause S_N2 reaction.

3. (b)

4. (a) : $C_4H_{10}O \xrightarrow{\text{excess of HI}}$ only RI

Since, the compound ($C_4H_{10}O$) does not react with sodium, oxygen must be in the form of ether (ROR). Further, since a single alkyl halide is formed, the two alkyl groups must be same, hence ether is $C_2H_5OC_2H_5$.

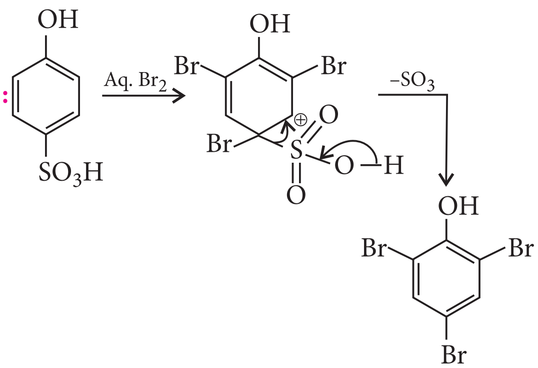
5. (b) :



Cu oxidises 2° alcohol to ketone

6. (c)

7. (b) :



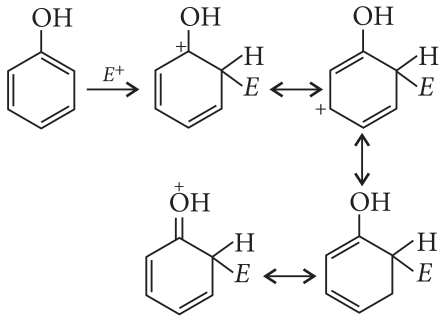
8. (b)

9. (c) : Phenols show keto-enol tautomerism and the stability of the keto form depends upon the number of keto groups (more the number of keto groups, higher will be stability of the keto tautomer). Thus, trihydric phenols should exist in keto form in considerable amount only when the two keto groups are not on adjacent carbon atoms.

10. (a) **11. (a,b)**

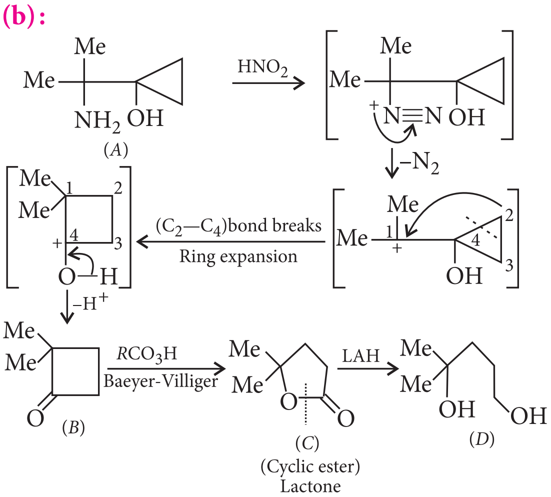
12. (b, d) **13. (b,d)** **14. (d)**

15. (c) :



Oxonium cation
(Every atom has complete octet)

16. (b) :



17. (c) **18. (c)** **19. (c)** **20. (b)**

21. (c) : Ethers being Lewis bases form etherates with Lewis acids.

22. (b) **23. (2)**

24. (2) : Williamson's synthesis requires that the alkyl halide should be 1° and alkoxide ion may be 1°, 2° or 3°. Thus, two ethers which cannot be prepared by Williamson's synthesis are :
$(C_6H_5)_2O$, $(CH_3)_3COC(CH_3)_3$.

25. (4) : MnO_2/CH_2Cl_2 can oxidise benzylic and allylic alcohols into carbonyl compounds while saturated alcohols remains unaffected. MnO_2 /CH_2Cl_2 can also oxidise alcoholic group adjacent to three membered ring and triple bond.

CLASS XII Series 4

ACE YOUR WAY CBSE

The *d*- and *f*-Block Elements Coordination Compounds

Time Allowed : 3 hours
Maximum Marks : 70

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
(iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
(v) Q. no. 23 is a value based question and carries 4 marks.
(vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

Previous Years Analysis

	2016		2015		2014	
	Delhi	AI	Delhi	AI	Delhi	AI
VSA	–	–	–	1	1	–
SA-I	2	1	2	1	1	–
SA-II	2	1	2	1	–	1
VBQ	–	–	–	–	–	–
LA	–	1	–	1	1	1

1. Transition elements show high melting points, why?

2. Why are low spin tetrahedral complexes not formed?

3. On what ground can you say that scandium ($Z = 21$) is a transition element but zinc ($Z = 30$) is not?

4. When a coordination compound $CrCl_3 \cdot 6H_2O$ is mixed with $AgNO_3$, 2 moles of AgCl are precipitated per mole of the compound. Write structural formula of the complex.

5. Why do transition elements show variable oxidation states?

6. A compound with the empirical formula $Co(NH_3)_5BrSO_4$ exists in two forms : red and violet. Red solution gives a precipitate of AgBr on addition of $AgNO_3$. The violet form gives no precipitate on the addition of $AgNO_3$ but gives a white precipitate on addition of $BaCl_2$ solution. From these observations draw the structure of each compound and explain the observations.

7. Identify *A* and *B* in the given sequence of reactions. Also, write their IUPAC names.

$$Fe^{3+}_{(aq)} \xrightarrow{\text{Excess of } SCN^-} \text{Blood red colour } (A) \xrightarrow{\text{Excess of } F^-} \text{Colourless } (B)$$

8. How would you account for the following :
(i) Transition elements have high enthalpies of atomisation.
(ii) Transition metals and their compounds are found to be good catalysts in many processes?

OR

Write the steps involved in the preparation of
(i) $K_2Cr_2O_7$ from $FeCr_2O_4$
(ii) $KMnO_4$ from K_2MnO_4

9. On the basis of crystal field theory, explain why Co(III) forms paramagnetic octahedral complexes with weak field ligands whereas it forms diamagnetic octahedral complexes with strong field ligands?

10. What is lanthanoid contraction? Mention its two consequences.

11. Draw the structures of optical isomers of each of the following complex ions :
$[Cr(C_2O_4)_3]^{3-}$, $[PtCl_2(en)_2]^{2+}$, $[Cr(NH_3)_2Cl_2(en)]^+$

12. What is meant by crystal field splitting energy? On the basis of crystal field theory, write the electronic configuration of d^4 in terms of t_{2g} and e_g in an octahedral field when **(i)** $\Delta_o > P$ **(ii)** $\Delta_o < P$

13. Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory :
(i) $[Fe(CN)_6]^{4-}$ **(ii)** $[FeF_6]^{3-}$ **(iii)** $[Co(C_2O_4)_3]^{3-}$

14. Compare the chemistry of the actinoids with that of lanthanoids with reference to **(i)** electronic configuration **(ii)** oxidation states **(iii)** chemical reactivity.

15. A violet compound (*A*) of manganese decomposes on heating to liberate oxygen and compound (*B*) and (*C*) of manganese are formed. Compound (*C*) reacts with KOH in the presence of potassium nitrate to give compound (*B*). On heating compound (*C*) with conc. H_2SO_4 and NaCl, chlorine gas is liberated and compound (*D*) of manganese along with other products is formed. Identify compounds (*A*) to (*D*) and also explain the reactions involved.

16.
$$\underset{\text{(colourless liquid, where } M \text{ is transition metal)}}{MCl_4} \xrightarrow{Zn} \underset{(A)}{\text{Purple coloured compound}}$$
$$MCl_4 \xrightarrow{\text{moist air}} \underset{(B)}{\text{White fumes}}$$

Identify (*A*), (*B*) and MCl_4. Also explain colour difference between MCl_4 and (*A*).

17. Write the IUPAC nomenclature of the following complex along with its hybridisation and structure.
$K_2[Cr(NO)(NH_3)(CN)_4]$, $\mu = 1.73$ BM

18. For the complex $[Fe(en)_2Cl_2]Cl$, identify the following :
(i) Oxidation number of iron
(ii) Hybrid orbitals and shape of the complex
(iii) Magnetic behaviour of the complex
(iv) Number of its geometrical isomers
(v) Whether there may be optical isomer also
(vi) Name of the complex

19. Give reasons for the following observations :
(i) Cu^+ ion is not stable in aqueous solution.
(ii) Mn(II) ion shows maximum paramagnetic character amongst the bivalent ions of first transition series.
(iii) Scandium (At. no. 21) salts are white.

OR

Complete the following chemical equations :
(i) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow$
(ii) $2CrO_4^{2-} + 2H^+ \rightarrow$
(iii) $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow$

20. (i) Using IUPAC norms write the formulae for the following coordination compounds :
(a) Hexaamminecobalt(III)chloride
(b) Potassiumtetrachloridonickelate(II)
(ii) What type of isomerism is exhibited by the complex $[Co(NH_3)_5NO_2]^{2+}$?

21. (i) Why is $[NiCl_4]^{2-}$ paramagnetic but $[Ni(CO)_4]$ is diamagnetic? (At. no. : Ni = 28)
(ii) What is meant by chelate effect ?

22. (i) Out of NH_3 and CO, which ligand forms a more stable complex with a transition metal and why?
(ii) What do you understand by stepwise stability constant and overall stability constant of a coordination compound? How are these two constants related?

23. Gaurav is a social worker. A farmer in the village had been complaining that a factory in his nearby area dumps chemical wastes in his fields which has become a major cause of decreasing productivity. Gaurav visited that place and found after analysis that the major waste was potassium permanganate which is being absorbed by the soil. He advised the factory people that they should treat potassium permanganate solution before dumping it.
(i) Comment in brief about the value/s displayed by Gaurav.
(ii) Write balanced chemical equations for the two reactions showing oxidizing nature of potassium permanganate.
(iii) Write any two uses of potassium permanganate in daily life.

24. (i) A blackish brown coloured solid '*A*' when fused with alkali metal hydroxides in presence of air, produces a dark green coloured compound *B*, which on electrolytic oxidation in alkaline medium gives a dark purple coloured compound *C*. Identify *A*, *B* and *C* and write the reactions involved.
(ii) What happens when an acidic solution of the green compound (*B*) is allowed to stand for some time? Give the equation involved. What is this type of reaction called ?

OR

Identify *A* to *E* and also explain the reactions involved.

$$CuCO_3 \rightarrow CuO \xrightarrow[\text{CuS}]{\text{heat with}} (A) \xrightarrow[\text{(conc.)}]{HNO_3} (B) \xrightarrow{NH_3(aq.)} \underset{\text{Blue solution}}{(C)}$$
$$CuCO_3 \rightarrow (D) \xrightarrow{Ca(OH)_2} \underset{\text{Milky}}{(E)} \xrightarrow{CO_2} \underset{\text{Clear solution}}{(F)}$$

25. (i) Using crystal field theory, draw energy level diagram, write electronic configuration of the central metal atom/ion and determine the magnetic moment value in the following :
(a) $[CoF_6]^{3-}$, (b) $[FeF_6]^{3-}$, (c) $[Fe(CN)_6]^{4-}$
(ii) $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution in 1:1 molar ratio gives the test of Fe^{2+} ion but $CuSO_4$ solution mixed with aqueous ammonia in 1 : 4 molar ratio does not give the test of Cu^{2+} ion. Explain why?

OR

(i) Using valence bond theory, explain the following in relation to the complexes given below :
$[Mn(CN)_6]^{3-}$, $[Co(NH_3)_6]^{3+}$, $[Cr(H_2O)_6]^{3+}$
(a) Type of hybridisation
(b) Inner or outer orbital complex
(c) Magnetic behaviour
(d) Spin only magnetic moment value
(ii) The colour of coordination compounds depends on the crystal field splitting. What will be the correct order of

absorption of wavelength of light in the visible region, for the complexes, $[Co(NH_3)_6]^{3+}$, $[Co(CN)_6]^{3-}$ and $[Co(H_2O)_6]^{3+}$.

26. On the basis of lanthanoid contraction, explain the following :

(i) Nature of bonding in La_2O_3 and Lu_2O_3

(ii) Trends in the stability of oxo salts of lanthanoids from La to Lu

(iii) Stability of the complexes of lanthanoids

(iv) Radii of 4*d* and 5*d* block elements

(v) Trends in acidic character of lanthanoid oxides.

OR

(i) When a chromite ore (*A*) is fused with sodium carbonate in free excess of air and the product is dissolved in water, a yellow solution of compound (*B*) is obtained. After treatment of this yellow solution with sulphuric acid, compound (*C*) can be crystallised from the solution. When compound (*C*) is treated with KCl, orange crystals of compound (*D*) crystallise out. Identify *A* to *D* and also explain the reactions.

(ii) $KMnO_4$ acts as an oxidising agent in acidic medium. Calculate the number of moles of $KMnO_4$ that will be needed to react with one mole of sulphide ions in acidic solution.

SOLUTIONS

1. High melting points of transition metals are attributed to the involvement of greater number of unpaired electrons in the interatomic metallic bonding from $(n - 1)\,d$ orbitals in addition to *ns* electrons.

2. Low spin tetrahedral complexes are not formed because of much smaller orbital splitting energies that are not enough to force pairing of electrons.

3. Scandium (Z = 21), atom has incompletely filled *d*-orbitals ($3d^1$) in its ground state whereas zinc ($Z = 30$) atom has completely filled *d*-orbitals ($3d^{10}$) in its ground state as well as in the most common oxidation state of +2.

4. For one mole of the compound, two moles of AgCl are precipitated which indicates that two ionisable chloride ions are present outside the coordination sphere. Hence, its structural formula is $[CrCl(H_2O)_5]Cl_2.H_2O$

5. Transition elements can use their *ns* and $(n - 1)d$ orbital electrons for bond formation therefore, they show variable oxidation states.

6. Red compound is $[Co(NH_3)_5SO_4]Br$.

It ionises to give Br^- ions in solution and therefore, form yellow ppt. of AgBr with $AgNO_3$ solution.

$$[Co(NH_3)_5SO_4]Br \rightleftharpoons [Co(NH_3)_5SO_4]^+ + Br^-$$

$$Br^- + AgNO_3 \rightarrow \underset{\text{Yellow ppt.}}{AgBr} + NO_3^-$$

Violet compound is $[Co(NH_3)_5Br]SO_4$. It ionises to give SO_4^{2-} ions which give white ppt. with $BaCl_2$ solution.

$$[Co(NH_3)_5Br]SO_4 \rightleftharpoons [Co(NH_3)_5Br]^{2+} + SO_4^{2-}$$

$$SO_4^{2-} + BaCl_2 \rightarrow \underset{\text{White ppt.}}{BaSO_4} + 2Cl^-$$

7. The given reactions sequence is

$$Fe^{3+}_{(aq)} \xrightarrow{SCN^-(\text{Excess})} \underset{\text{Blood red colour }(A)}{Fe(SCN)_3} \xrightarrow{F^-(\text{Excess})} \underset{\text{Colourless }(B)}{[FeF_6]^{3-}}$$

A - Trithiocyanoferrum (III), *B* - Hexafluoroferrate (III) ion

8. (i) As transition elements have a large number of unpaired electrons in the *d*-orbitals, they have strong interatomic attractions or metallic bonds. Hence, they have high enthalpy of atomisation.

(ii) Transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant(s) and ability to form complexes. Vanadium (V) oxide (in Contact process), finely divided iron (in Haber's process), and nickel (in catalytic hydrogenation) are some of the examples.

OR

(i) $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

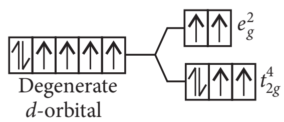
$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$

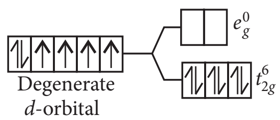
(ii) The potassium manganate is oxidised to potassium permanganate by oxidation with chlorine.

$2K_2MnO_{4(aq)} + Cl_{2(g)} \longrightarrow 2KMnO_{4(aq)} + 2KCl_{(aq)}$

9. For weak field ligands $\Delta_o < P$ (pairing energy), so pairing does not occur and the electronic configuration of Co (III) is $t_{2g}^4\,e_g^2$, *i.e.*, it has 4 unpaired electrons and is paramagnetic.



For strong field ligands Δ_o > P (pairing energy), so pairing occurs and the electronic configuration of Co (III) is $t_{2g}^6\,e_g^0$, *i.e.*, it has no unpaired electrons and is diamagnetic.



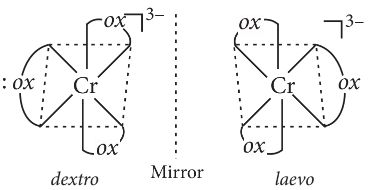
10. Lanthanoid contraction : The steady decrease in the atomic and ionic radii of lanthanoid elements with increase in atomic number due to imperfect shielding of nuclear charge by 4*f*-electrons is called lanthanoid contraction.

Consequences of lanthanoid contraction :

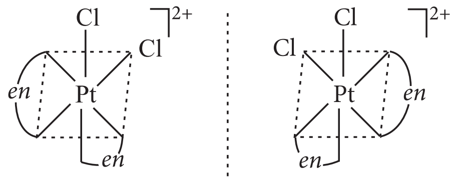
(i) The basic strength of oxides and hydroxides of lanthanoids decreases with increasing atomic number.

(ii) Atomic and ionic sizes of 4*d* transition series elements and 5*d* series elements are similar, *e.g.*, atomic radii of zirconium(Zr) is same as that of hafnium Hf.

11. $[Cr(C_2O_4)_3]^{3-}$:

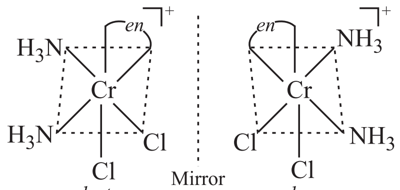


$[PtCl_2(en)_2]^{2+}$:



dextro Mirror *laevo*

$[Cr(NH_3)_2Cl_2(en)]^+$:



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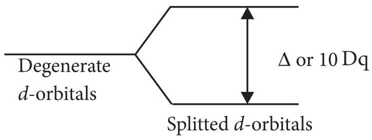
12. The difference of energy between the two states of splitted *d*-orbitals is called crystal field splitting energy. It is denoted by Δ or 10 Dq.

For octahedral it is Δ_o, for tetrahedral it is Δ_t and for square planar Δ_{sp}.



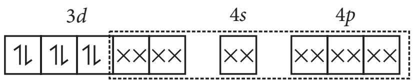
(i) When $\Delta_o > P$, $t_{2g}^4\, e_g^0$.

(ii) When $\Delta_o < P$, $t_{2g}^3\, e_g^1$.

13. (i) $[Fe(CN)_6]^{4-}$: Fe(26) – [Ar] $3d^6 4s^2$; Fe^{2+} ion – [Ar] $3d^6 4s^0$

CN^- ion causes pairing of electrons because it is a strong field ligand.

$[Fe(CN)_6]^{4-}$:



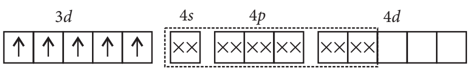
d^2sp^3 hybridisation

It has octahedral shape and is diamagnetic in nature due to absence of unpaired electrons.

(ii) $[FeF_6]^{3-}$: Fe(26) – [Ar] $3d^6 4s^2$; Fe^{3+} – [Ar] $3d^5 4s^0$

F^- being a weak field ligand, does not cause pairing of electrons.

$[FeF_6]^{3-}$:

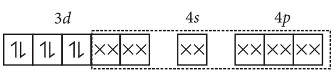


sp^3d^2 hybridisation, octahedral shape

(iii) $[Co(C_2O_4)_3]^{3-}$: Co(27) – [Ar] $3d^7 4s^2$; Co^{3+} – [Ar] $3d^6 4s^0$

$C_2O_4^{2-}$ being a strong field ligand causes pairing of electrons.

$[Co(C_2O_4)_3]^{3-}$



d^2sp^3 hybridisation, octahedral shape

14. (i) Electronic configuration : The general electronic configuration of lanthanoids is [Xe] $4f^{1-14}\, 5d^{0-1}\, 6s^2$ where as that of actinoids is [Rn] $5f^{1-14}\, 6d^{0-1}\, 7s^2$. Thus, lanthanoids involve the filling of 4*f*-orbitals whereas actinoids involve the filling of 5*f*-orbitals.

(ii) Oxidation states : Lanthanoids have principal oxidation state of +3. In addition, lanthanoids show limited oxidation states such as +2, and +4 because of large energy gap between 4*f* and 5*d* subshells. On the other hand, actinoids show a large number of oxidation states because of small energy gap between 5*f* and 6*d* subshells.

(iii) Chemical reactivity :

(a) First few members of lanthanoids are quite reactive almost like calcium but reactivity decreases with increase in atomic number whereas actinoids are highly reactive metals especially in the finely divided state.

(b) Lanthanoids react with dilute acids to liberate H_2 gas whereas actinoids react with boiling water to give a mixture of oxide and hydride.

15. Since, compound *C* on treating with conc. H_2SO_4 and NaCl gives Cl_2 gas, so it is manganese dioxide (MnO_2). It is obtained alongwith MnO_4^{2-} when $KMnO_4$ (violet) is heated.

Thus, $A = KMnO_4$, $B = K_2MnO_4$, $C = MnO_2$, $D = MnCl_2$

$$\underset{A}{2KMnO_4} \xrightarrow{\Delta} \underset{B}{K_2MnO_4} + \underset{C}{MnO_2} + O_2$$

$$\underset{C}{MnO_2} + 2KOH + KNO_3 \longrightarrow \underset{B}{K_2MnO_4} + H_2O + KNO_2$$

$$\underset{C}{MnO_2} + 4NaCl + \underset{(conc.)}{4H_2SO_4} \longrightarrow \underset{D}{MnCl_2} + 4NaHSO_4 + 2H_2O + Cl_2$$

16. $MCl_4 = TiCl_4$ (colourless, diamagnetic)

$$TiCl_{4(aq)} \underset{\Delta}{\xrightarrow{Zn}} TiCl_3 \xrightarrow{H_2O} \underset{\text{Purple coloured }(A)}{[Ti(H_2O)_6]Cl_3}$$

(Reduction)

$$TiCl_4 + H_2O \longrightarrow TiOCl_2 + \underset{\text{White fumes }(B)}{2HCl}$$

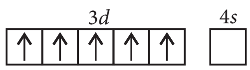
Hence, $A = [Ti(H_2O)_6]Cl_3$, $B = HCl$, $MCl_4 = TiCl_4$

Colour difference : $TiCl_4$ is colourless because Ti (IV) has empty *d*-subshell. Hence, no *d-d* transition is possible. Ti (III) has d^1 configuration hence, Ti(III) is coloured due to *d-d* transition. Ti^{3+} absorbs greenish yellow component of white light. The complementary colour is purple. Hence, aqueous solution containing Ti^{3+} ions is purple.

17. $\mu = \sqrt{n(n+1)} = 1.73$ which gives $n = 1$

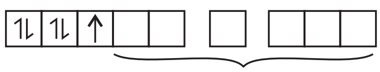
This means that chromium ion has one unpaired electron, *i.e.*, it is present as Cr^+ or Cr (I). This implies that NO is present as nitrosonium ion. Hence, the name will be potassium ammine tetracyanonitrosonium chromate (I).

Cr^+ :



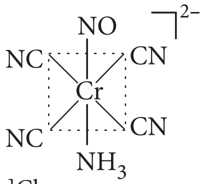
In the complex, as there is only one unpaired electron and coordination number is 6, it will become

Cr^+ :



d^2sp^3 hybridisation

i.e., it will undergo d^2sp^3 hybridisation to give octahedral geometry.

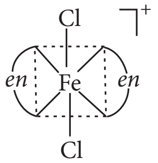


18. (i) $[Fe(en)_2Cl_2]Cl$:
$x + 0 \times 2 + (-1) \times 2 + (-1) \times 1 = 0 \ \therefore x = 3$
Oxidation number of iron = 3

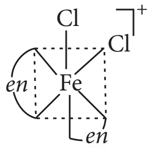
(ii) d^2sp^3 hybridisation and octahedral shape.

(iii) Paramagnetic due to presence of one unpaired electron.

(iv) 2, *cis* and *trans* isomers.

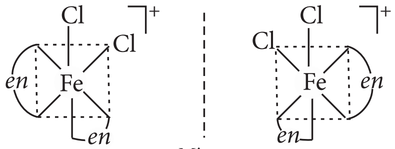


Trans-dichloridobis(ethane-1, 2-diamine)iron(III) chloride



Cis-dichloridobis(ethane-1, 2-diamine)iron(III) chloride

(v) *cis*-$[Fe(en)_2Cl_2]^+$ has optical isomer (*dextro* and *laevo*).



dextro Mirror *laevo*

(vi) dichlorido*bis*(ethane-1,2-diamine)iron(III)chloride

19. (i) In aqueous solutions, Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.

$2Cu^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$

Cu^{2+} in aqueous solutions is more stable than Cu^+ ion because hydration enthalpy of Cu^{2+} is higher than that of Cu^+. It compensates the second ionisation enthalpy of Cu involved in the formation of Cu^{2+} ions.

(ii) This is due to the presence of maximum number of unpaired electrons in Mn^{2+} ($3d^5$).

(iii) Only those ions are coloured which have partially filled *d*-orbitals facilitating *d-d* transitions.
However, in case of Sc as the *d*-orbital is empty after the formation of compound, there is no *d-d* transition. Thus, the compounds appear white.

OR

(i) $Cr_2O^{2-}_{7(aq)} + 14H^+_{(aq)} + 6Fe^{2+}_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)} + 6Fe^{3+}_{(aq)} + 7H_2O_{(l)}$

(ii) $2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$

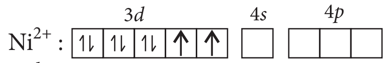
(iii) $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

20. (i) (a) $[Co(NH_3)_6]Cl_3$

(b) $K_2[NiCl_4]$

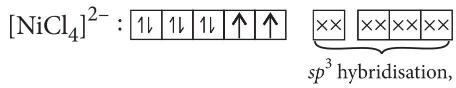
(ii) Linkage isomerism : $[Co(NH_3)_5NO_2]^{2+}$ and $[Co(ONO)(NH_3)_5]^{2+}$

21. (i) $[NiCl_4]^{2-}$ contains Ni^{2+} ion with $3d^8$ configuration.

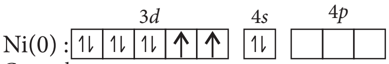


Ground state

Cl^- is a weak field ligand. Hence, outer 4*s* and 4*p*-orbitals are used in hybridisation.



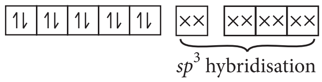
It has two unpaired electrons hence, it is paramagnetic.
$[Ni(CO)_4]$ contains Ni(0) – $3d^84s^2$ configuration.



Ground state

CO is a strong field ligand hence, 4*s*-electrons will shift to 3*d*-orbital making 4*s*-orbital vacant.

$[Ni(CO)_4]$:



The complex has all paired electrons hence, it is diamagnetic.

(ii) When a di - or poly-dentate ligand uses its two or more donor atoms to bind a single metal ion. It is said to be a chelate ligand. Chelating ligands form more stable complexes than *mono* dentate ligands. This is called chelating effect.

22. (i) In CO both lone pair of electrons and vacant π^*-orbitals are present. Hence, it acts as electron pair σ-donor as well as π-acceptor by back bonding. Hence, *M*—CO bond is stronger. $M \underset{\sigma}{\overset{\pi}{\rightleftarrows}} CO$

NH_3 is electron pair donor only. Accumulation of negative charge on the metal ion takes place, hence M—NH_3 bond is weaker.

(ii) Stability constant of each step of complex formation reaction is called stepwise stability constant. It is denoted by *K*. Stability constant of overall complex formation reaction is called overall stability constant. It is denoted by β.
The stepwise and overall stability constant are therefore related as follows :
$\beta_4 = K_1 \times K_2 \times K_3 \times K_4$ or more generally,
$\beta_n = K_1 \times K_2 \times K_3 \times K_4 \ldots K_n$

23. (i) The values displayed by Gaurav are social responsibility and scientific knowledge.

(ii) (a) Oxidation of oxalate ion into CO_2,

$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

(b) Oxidation of nitrite into nitrate,

$5NO_2^- + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$

(iii) It is widely used as a disinfectant and germicide.

24. (i)

$\underset{\text{Pyrolusite (A) – Blackish brown}}{MnO_2} + 4KOH + O_2 \xrightarrow{\text{Fuse}} \underset{\text{Potassium manganate (B) – Green coloured}}{2K_2MnO_4} + 2H_2O$

$$2K_2MnO_4 + H_2O + (O) \xrightarrow[\text{medium}]{\text{Alkaline}} 2KMnO_4 + 2KOH$$

(B) ; $2KMnO_4$: Potassium permanganate (C)–Purple coloured

or $\quad MnO_4^{2-} \longrightarrow MnO_4^- + e^-$

(ii) When acidic solution of green compound (B), *i.e.*, potassium manganate is allowed to stand for some time, it disproportionates to give permanganate as follows :

$$\underset{(B)}{3MnO_4^{2-}} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

This reaction is called disproportionation reaction.

OR

$$\underset{(D)}{CuCO_3 \rightarrow CuO + CO_2}$$

$$CuO + CuS \rightarrow \underset{(A)}{Cu} + SO_2$$

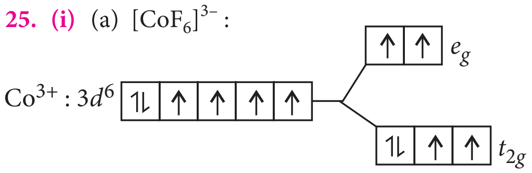
$$\underset{(A)}{Cu} + 4HNO_3\,(\text{conc.}) \rightarrow \underset{(B)}{Cu(NO_3)_2} + 2NO_2 + 2H_2O$$

$$\underset{(B)}{Cu^{2+}} + 4NH_{3(aq)} \rightarrow \underset{\substack{(C)\\ \text{(Blue solution)}}}{[Cu(NH_3)_4]^{2+}}$$

$$Ca(OH)_2 + \underset{(D)}{CO_2} \rightarrow \underset{\substack{(E)\\ \text{(Milky)}}}{CaCO_3} + H_2O$$

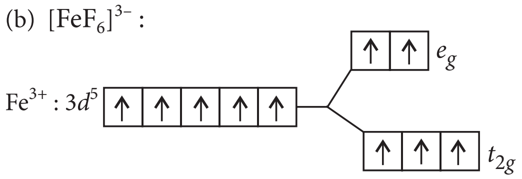
$$CaCO_3 + H_2O + CO_2 \rightarrow \underset{\substack{(F)\\ \text{(Clear solution)}}}{Ca(HCO_3)_2}$$

25. (i) (a) $[CoF_6]^{3-}$:



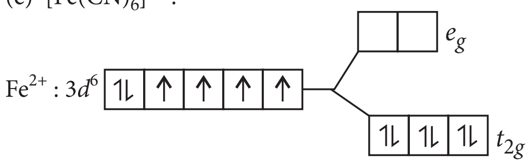
No. of unpaired electrons = 4, $\mu = \sqrt{4(4+2)} = 4.9$ B.M.

(b) $[FeF_6]^{3-}$:



No. of unpaired electrons = 5, $\mu = \sqrt{5(5+2)} = 5.92$ B.M.

(c) $[Fe(CN)_6]^{4-}$:



No. of unpaired electrons = 0, $\mu = 0$

(ii) When $FeSO_4$ and $(NH_4)_2SO_4$ solutions are mixed in 1 : 1 molar ratio, Mohr's salt (a double salt) is formed.

$$FeSO_{4(aq)} + (NH_4)_2SO_{4(aq)} \rightarrow FeSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$$

$$FeSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O \rightleftharpoons Fe^{2+}_{(aq)} + 2NH^+_{4(aq)} + 2SO^{2-}_{4(aq)} + 6H_2O$$

Because Fe^{2+} ions are formed on dissolution of Mohr's salt, its aqueous solution gives the test of Fe^{2+} ions.

When $CuSO_4$ is mixed with ammonia, following reaction occurs :

$$CuSO_{4(aq)} + 4NH_{3(aq)} \rightarrow [Cu(NH_3)_4]SO_4$$

This complex does not produce Cu^{2+} ion, so the solution of $CuSO_4$ and NH_3 does not give the test of Cu^{2+} ion.

OR

(i) $[Mn(CN)_6]^{3-}$:

	3d					4s	4p		
$Mn^{3+}(3d^4)$:	⇅	↑	↑	××	××	××	××	××	××

(a) Hybridisation - d^2sp^3 (b) Inner orbital complex

(c) Paramagnetic (d) $\mu = \sqrt{2(2+2)} = 2.87$ B.M.

$[Co(NH_3)_6]^{3+}$:

	3d					4s	4p		
$Co^{3+}(3d^6)$:	⇅	⇅	⇅	××	××	××	××	××	××

(a) Hybridisation - d^2sp^3 (b) Inner orbital complex

(c) Diamagnetic (d) Magnetic moment = 0

$[Cr(H_2O)_6]^{3+}$:

	3d					4s	4p		
$Cr^{3+}(3d^3)$:	↑	↑	↑	××	××	××	××	××	××

(a) Hybridisation - d^2sp^3 (b) Inner orbital complex

(c) Paramagnetic (d) $\mu = \sqrt{3(3+2)} = 3.87$ B.M.

(ii) Strong field ligands split the five degenerate energy levels with more energy separation than weak field ligands, *i.e.*, as strength of ligand increases crystal field splitting energy increases. Hence, $\Delta E = \frac{hc}{\lambda} \Rightarrow \Delta E \propto \frac{1}{\lambda} \Rightarrow \lambda \propto \frac{1}{\Delta E}$

As energy separation increases, the wavelength decreases.

Thus, the correct order is

$[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$

26. (i) As the size decreases covalent character increases. Therefore, La_2O_3 is more ionic and Lu_2O_3 is more covalent.

(ii) As the size decreases from La to Lu, stability of oxosalts also decreases.

(iii) Stability of complexes increases as the size decreases.

(iv) Radii of 4*d* and 5*d* block elements will almost be same. The filling of 4*f* before 5*d* results in lanthanoid contraction hence, 4*d* and 5*d* series have almost same size.

(v) Acidic character of oxides increases from La to Lu.

OR

(i) $$\underset{(A)}{4FeCr_2O_4} + 8Na_2CO_3 + 7O_2 \longrightarrow \underset{(B)}{8Na_2CrO_4} + 2Fe_2O_3 + 8CO_2$$

$$\underset{(B)}{2Na_2CrO_4} + 2H^+ \longrightarrow \underset{(C)}{Na_2Cr_2O_7} + 2Na^+ + H_2O$$

$$\underset{(C)}{Na_2Cr_2O_7} + 2KCl \longrightarrow \underset{(D)}{K_2Cr_2O_7} + 2NaCl$$

(ii) $2KMnO_4 + 3H_2SO_4 + 5H_2S \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5S$

5 moles of S^{2-} ions react with 2 moles of $KMnO_4$. So, 1 mole of S^{2-} ion will react with 2/5 moles of $KMnO_4$.

MPP-3 MONTHLY Practice Problems

Class XII

This specially designed column enables students to self analyse their extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer.

Self check table given at the end will help you to check your readiness.

Surface Chemistry | Chemical Kinetics

Total Marks : 120 **Time Taken : 60 Min.**

NEET / AIIMS

Only One Option Correct Type

1. For a reaction $A_2 + B_2 \longrightarrow 2AB$, evaluate the energy of activation from the following data :

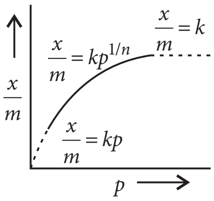
T (in K)	$1/T$ (K^{-1})	$\log_{10} k$
500	2×10^{-3}	3.0
200	5×10^{-3}	2.0

(a) 15.4 kcal (b) 1.54 kcal
(c) 154 kcal (d) 1.54×10^3 kcal

2. Which one is incorrect about positive catalyst or negative catalyst?
(a) Positive catalyst lowers the energy of activation.
(b) Negative catalyst increases the energy of activation.
(c) Positive catalyst increases the rate of reaction.
(d) Negative catalyst functions to remove active intermediates.

3. The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the pre-exponential factor for the reaction is 3.56×10^9 s^{-1}, calculate its rate constant at 318 K.
(a) 0.92×10^{-4} sec^{-1} (b) 9.22×10^{-4} sec^{-1}
(c) 92.2×10^{-4} sec^{-1} (d) 92×10^{-4} sec^{-1}

4. Which one is not correct about Freundlich isotherm?



(a) $n = \dfrac{1}{\tan\theta}$ at average pressure
(b) $\theta = 45°$ at low pressure
(c) $\theta = 45°$ at high pressure
(d) None of these

5. For a reaction $A \longrightarrow$ Products, starting with initial concentrations of 5×10^{-3} M and 25×10^{-4} M, half- lives are found to be 1.0 and 8.0 hour respectively. If we start with an initial concentration of 1.25×10^{-3} M, the half life of the reaction will be
(a) 16 h (b) 32 h (c) 64 h (d) 256 h

6. When the concentration of 'A' is 0.1 M, it decomposes to give 'X' by a first order process with a rate constant of 6.93×10^{-2} min^{-1}. The reactant 'A' in the presence of catalyst gives 'Y' by a second order mechanism with a rate constant of 0.2 min^{-1} M^{-1}. In order that half life of both the processes be 10 minutes, one should start with an initial concentration of 'A' as
(a) 0.01 M (b) 5.0 M (c) 10.0 M (d) 0.5 M

7. A colloidal solution is subjected to an electric field. The particles move towards anode. The coagulation of same sol is studied using NaCl, $BaCl_2$ and $AlCl_3$ solutions. Their coagulating power should be
(a) NaCl > $BaCl_2$ > $AlCl_3$ (b) $BaCl_2$ > $AlCl_3$ > NaCl
(c) $AlCl_3$ > $BaCl_2$ > NaCl (d) $BaCl_2$ > NaCl > $AlCl_3$

8. Which of the following is less than zero during adsorption?
(a) ΔG (b) ΔS (c) ΔH (d) All of these.

9. During nuclear explosion one of the products is ^{90}Sr with half-life of 28.1 years. If 1 μ g of ^{90}Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 60 yr if it is not lost metabolically?
(a) 0.184 μg (b) 0.025 μg (c) 0.262 μg (d) 0.228 μg

10. Which of the following statements are correct?
1. Order of a reaction can be known from experimental result and not from the stoichiometry of reaction.
2. Overall molecularity of a reaction may be determined in a manner similar to overall order of reaction.
3. Overall order of reaction, $A^m + B^n \longrightarrow AB_x$ is $(m + n)$
4. Molecularity of a reaction refers to
   (i) molecularity of each of the elementary steps (slow steps) in a multistep reaction.
   (ii) molecularity of that particular step in a single step reaction.

(a) 1, 3 and 4 (b) 1, 2 and 3
(c) 2, 3 and 4 (d) 1, 2 and 4

11. Plot of $\log \frac{x}{m}$ against $\log p$ is a straight line inclined at an angle of 45°. When the pressure is 0.5 atm and Freundlich parameter, k is 10, the amount of solute adsorbed per gram of adsorbent will be ($\log 5 = 0.6990$)
(a) 1 g (b) 2 g (c) 3 g (d) 5 g

12. 50 mL of 1 M oxalic acid is shaken with 0.5 g wood charcoal. The final concentration of the solution after adsorption is 0.5 M. What is the amount of oxalic acid absorbed per gram of carbon?
(a) 3.15 g (b) 3.45 g
(c) 6.30 g (d) None of these

Assertion & Reason Type

Directions : In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :
(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

13. Assertion : Rate constants determined from Arrhenius equation are fairly accurate for simple as well as complex molecules.
Reason : Reactant molecules undergo chemical change irrespective of their orientation during collision.

14. Assertion : The micelles formed by sodium stearate in water has $-COO^-$ groups at the surface.
Reason : Surface tension of water is increased by the addition of sodium stearate.

15. Assertion : 50% of a zero order reaction is completed in 100 sec, therefore, 75% reaction will be completed in 150 sec.
Reason : The rate constant of a zero order reaction depends upon time.

JEE MAIN / JEE ADVANCED / PETs

Only One Option Correct Type

16. In the Arrhenius equation for a certain reaction, the values of A and E_a (energy of activation) are 4×10^{13} sec^{-1} and 98.6 kJ mol^{-1} respectively. If the reaction is of first order, at what temperature will its half life period be 10 minute?
(a) 31.35 K (b) 311.35 K (c) 3.11 K (d) 31.34 K

17. The lowering of activation energy by catalyst is due to
(a) formation of adsorbed activated complex and to provide new pathway to reaction
(b) adsorption is always exothermic
(c) the adsorbed activated complex possesses lower energy level than simple activated complex
(d) all of the above.

18. Two substances A and B are present together such that $[A]_0 = 4[B]_0$. Half-lives of A and B are 5 minutes and 15 minutes respectively. If they start decaying at the same time each following first order kinetics, the time after which their concentrations become equal would be
(a) 15 min (b) 60 min (c) 30 min (d) 40 min

19. Which one of the following statements about the zeolites is false?
(a) They are used as cation exchangers.
(b) They have open structure which enables them to take up small molecules.
(c) Zeolites are aluminosilicates having three-dimensional network.
(d) Some of the SiO_4^{4-} units are replaced by AlO_4^{5-} and AlO_6^{9-} ions in zeolites.

More than One Options Correct Type

20. Consider the following case of completing first order reactions : $A \begin{cases} \xrightarrow{k_1} B \\ \xrightarrow{k_2} C \end{cases}$
After the start of the reaction at $t = 0$ with only A, the $[B]$ is equal to the $[C]$ at all times.
The time in which all three concentrations will be equal is given by
(a) $t = \frac{1}{3k_1}\ln 2$ (b) $t = \frac{1}{2k_1}\ln 3$
(c) $t = \frac{1}{3k_2}\ln 2$ (d) $t = \frac{1}{2k_2}\ln 3$

21. When a hydrophilic sol like gelatin is subjected to electric field, the sol particles move
(a) towards cathode at pH less than the iso-electric point
(b) towards anode at pH greater than the iso-electric point
(c) in both directions at iso-electric pH
(d) in neither direction at iso-electric pH.

22. Which of the following statements are correct?
(a) Colloidal electrolytes are those electrolytes that are partially associated and that form conducting micelles.
(b) Dyes and soaps belong to colloidal electrolytes.
(c) The solutions of colloidal electrolytes have higher osmotic pressure than expected.
(d) Colloidal electrolytes can be regarded as macromolecules.

23. Which of the following statements are correct?
(a) Time required for 75% completion is 1.5 times of half-life for zero order reaction.
(b) Time required for a definite fraction of first order reaction does not vary with the initial concentration.
(c) Time for 25% reaction is one-third of half-life in second order process.

(d) Rate of zero order reaction gets doubled if the concentration of the reactant is increased to a two fold value.

Integer Answer Type

24. The rate constant (k) for the reaction,
$2A + B \longrightarrow$ Product, was found to be
2.5×10^{-5} litre mol^{-1} s^{-1} after 15 seconds, 2.60×10^{-5} litre mol^{-1} s^{-1} after 30 seconds and 2.55×10^{-5} litre mol^{-1} s^{-1} after 50 seconds. The order of reaction is

25. Among the given sols, the number of sols that can coagulate silicic acid sol is
$Fe(OH)_3$, $Ca(OH)_2$, $Al(OH)_3$, starch, clay, As_2S_3, basic dye , CdS

26. In the following reaction, the initial concentrations of the reactant and initial rate at 298 K are given
$2A \longrightarrow C + D$

$[A]_0$, mol L^{-1}	Initial rate in mol L^{-1} s^{-1}
0.01	5.0×10^{-5}
0.02	2.0×10^{-4}

The rate constant of this reaction at 298 K is $x \times 10^{-1}$ mol^{-1} L s^{-1}. The value of x is

Comprehension Type

Chemical reactions such as, $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ which proceed from reactants to products through one or more intermediate steps are called consecutive reactions. In these reactions each stage has its own rate and own rate constant. The simplest case is one in which there are only two consecutive stages and the two reactions are of the first order with specific reaction rates k_1 and k_2.

$$[A]_t = [A]_0 \cdot e^{-k_1 \cdot t}; \text{ and } [B] = \frac{k_1[A]_0}{k_2 - k_1}(e^{-k_1 \cdot t} - e^{-k_2 \cdot t})$$

27. The above equation shows that
(a) concentration of A falls exponentially and the amount of C will rise until it approaches that of B.
(b) concentration of A falls exponentially but the concentration of B slowly goes on increasing till it becomes constant at certain concentrations.
(c) The concentration of B first increases and rises to a maximum and then decreases.
(d) all the above are correct.

28. The time (t) when B is present in maximum concentration is given by
(a) $t = \frac{k_1}{k_2 - k_1}$
(b) $t = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$
(c) $\frac{1}{k_2 - k_1} \ln \frac{k_1}{k_2}$
(d) none of these.

Matrix Match Type

29. Match the entries listed in Column I with appropriate entries listed in Column II.

Column I	Column II
(A) Reactions of zero order	(P) Rate constant has the units L mol^{-1} s^{-1}
(B) Reactions of Ist order	(Q) Half-life period is directly proportional to initial concentration
(C) Reactions of 2nd order	(R) Example is reaction of acetic anhydride with excess of ethanol
(D) Pseudounimolecular reaction	(S) Percent dissociation of the reactant at time $t = (1 - e^{-kt}) \times 100$

	A	B	C	D
(a)	Q	S	P	R
(b)	P	S	Q	R
(c)	P	Q	R	S
(d)	Q	P	S	R

30. Match the entries listed in Column I with appropriate entries listed in Column II.

Column I	Column II
(A) $AgNO_{3(aq)}$ + little excess of KI	(P) Sol particles migrate towards cathode under electric field
(B) $KI_{(aq)}$ + little excess of $AgNO_3$	(Q) Sol particles migrate towards anode under electric field
(C) Gelation sol at pH < isoelectric pH	(R) Sol particles are negatively charged
(D) Protein sol at pH > isoelectric pH	(S) Sol particles carry positive charge

	A	B	C	D
(a)	P,Q	S	Q,R	P,Q
(b)	P,Q,R	P,Q,S	Q	R
(c)	S,Q	P,S	P,Q	R,Q
(d)	Q,R	P,S	P,S	Q,R

◈◈

Keys are published in this issue. Search now! ☺

SELF CHECK

No. of questions attempted ……
No. of questions correct ……
Marks scored in percentage ……

Check your score! If your score is

> 90%	EXCELLENT WORK !	You are well prepared to take the challenge of final exam.
90-75%	GOOD WORK !	You can score good in the final exam.
74-60%	SATISFACTORY !	You need to score more next time.
< 60%	NOT SATISFACTORY!	Revise thoroughly and strengthen your concepts.

CHEMISTRY MUSING

Chemistry Musing was started from August '13 issue of Chemistry Today with the suggestion of Shri Mahabir Singh. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / NEET / AIIMS / PMTs with additional study material.

In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / NEET. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue.

We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

PROBLEM Set 38

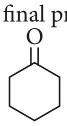
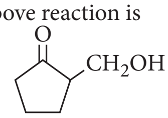
JEE MAIN/NEET

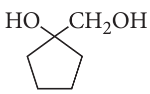
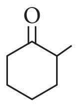
1. An aeroplane weighing 63,000 kg flies up from sea level to a height of 8000 m. It's engine run with pure normal octane (C_8H_{18}) has a 40% efficiency. What is the fuel cost of the flight (in ₹), if octane sells at ₹ 3 per litre? [Density of octane = 0.705 g mL^{-1}, heat of combustion of octane = 1300 kcal mol^{-1}, (g = 981 cm/sec^2)]
(a) 1472.4 (b) 1101.9 (c) 14.72 (d) 10.97

2. An organic liquid A, (immiscible with water) when boiled together with water, the boiling point is 90°C at which the partial vapour pressure of water is 526 mm Hg. The atmospheric pressure is 736 mm Hg. The weight ratio of the liquid and water collected is 2.5 : 1. The molecular weight of the liquid is
(a) 112.7 g mol^{-1} (b) 11.27 g mol^{-1}
(c) 117.2 g mol^{-1} (d) 121.7 g mol^{-1}

3. $\underset{\text{(Cyclopentanone)}}{C_5H_8O} \xrightarrow[\text{pH 9–10}]{HCN} (A) \xrightarrow[\text{Ether}]{LiAlH_4} (B) \xrightarrow[HCl]{NaNO_2} (C)$

The final product (C) in the above reaction is

(a)  (b) 

(c)  (d) 

4. A colourless inorganic salt (A) decomposes completely at about 523 K to give only two products (B) and (C) leaving no residue. The product (B) is a neutral gas while the product (C) is liquid at room temperature and is neutral to litmus. White phosphorus burns in excess of (B) to produce a strong dehydrating agent P_4O_{10}. The compounds (A), (B) and (C) are respectively
(a) NH_4NO_2, N_2, H_2O (b) NH_4NO_3, N_2O, H_2O
(c) NH_4Cl, NH_3, HCl (d) $NaNO_3$, O_2, $NaNO_2$

5. 18 mL of iodine and 25 mL of hydrogen when heated in a closed container, produced 30.8 mL of HI at equilibrium. The degree of dissociation of HI at the same temperature is
(a) 0.245 (b) 2.45 (c) 2.045 (d) 24.5

JEE ADVANCED

6. An alkyl bromide (A) was treated with excess of ammonia to give (B) as the major product. (B) was subsequently treated with one equivalent of CH_3I to give (C). (B) and (C) on treating with aqueous $NaNO_2$ and HCl give compounds (D) and (E) respectively. (D) on oxidation followed by decarboxylation gives ethane. The structure of the compond (E) is
(a) $CH_3CH_2CH_2CH_2-N(N{=}O)-CH_3$
(b) $CH_3CH_2-N(N{=}O)-CH_3$ (c) $(CH_3)_2CHCH_2-N(N{=}O)-CH_3$
(d) $CH_3CH_2CH_2-N(N{=}O)-CH_3$

COMPREHENSION

Copper is extracted from copper pyrites. After roasting, the ore is smelted in presence of silica and coke in a blast furnace. The molten matte obtained from the blast furnace is taken into Bessemer converter. Some silica is also added and a hot air blast is blown into the mixture to obtain blister copper which is purified by electrorefining.

7. During roasting, copper pyrites are converted into a mixture of
(a) CuS + Fe_2S_3 (b) Cu_2S + FeS
(c) $CuSO_4$ + FeS (d) Cu_2S + $FeSO_4$

8. Identify the metal 'M' in the following reactions :
$M_2S + O_2 \longrightarrow M_2O$; $M_2S + M_2O \longrightarrow M$. The metal M is
(a) iron (b) copper (c) zinc (d) mercury.

INTEGER VALUE

9. Analysis shows that a metal oxide has the empirical formula $M_{0.97}O_{1.00}$ where M is present in +2 and +3 oxidation states. The percentage of M present as M^{3+} is

10. The value of x obtained when H—O—O bond angle in H_2O_2 is subtracted from 100 *i.e.*, x = 100 – (H—O—O bond angle) is

NEET

SOLVED PAPER 2016

Phase-II held on 24th July

Hurray!! We are happy to inform our readers that out of the 45 questions asked in NEET 2016, more than 60% questions were either exactly same or of similar type from the **MTG Books.** Hurray!!

Here, the references of few are given :

S. No.	MTG Books	Q. No.	Pg. No.	S. No.	MTG Books	Q. No.	Pg. No.
1	NCERT Fingertips (XI)	96	69	14	NEET Guide	91	12
2	NCERT Fingertips (XII)	43	54	15	Objective Chemistry	11	679
4	Objective Chemistry	87	762	16	NEET Guide	7	300
6	Objective Chemistry	35	66	19	NCERT Fingertips (XI)	15	191
9	Objective Chemistry	201	310	20	NCERT Fingertips	3	70
10	NCERT Fingertips (XII)	24	7	22	NEET Guide	144	99
11	NEET Guide	18	498	23	NCERT Fingertips (XI)	85	188
12	NEET Guide	21	464	26	Objective Chemistry	268	163
13	NCERT Fingertips (XI)	94	130	36	NEET Guide	114	798

and more such questions ......

1. Which one of the following compounds shows the presence of intramolecular hydrogen bond?
(a) H_2O_2 (b) HCN
(c) Cellulose (d) Concentrated acetic acid

2. The molar conductivity of a 0.5 mol/dm^3 solution of $AgNO_3$ with electrolytic conductivity of 5.76×10^{-3} S cm^{-1} at 298 K in S cm^2/mol is
(a) 2.88 (b) 11.52 (c) 0.086 (d) 28.8

3. The decomposition of phosphine (PH_3) on tungsten at low pressure is a first-order reaction. It is because the
(a) rate is proportional to the surface coverage
(b) rate is inversely proportional to the surface coverage
(c) rate is independent of the surface coverage
(d) rate of decomposition is very slow.

4. The coagulation values in millimoles per litre of the electrolytes used for the coagulation of As_2S_3 are given : I. (NaCl) = 52, II. ($BaCl_2$) = 0.69, III. ($MgSO_4$) = 0.22. The correct order of their coagulating power is
(a) I > II > III (b) II > I > III
(c) III > II > I (d) III > I > II

5. During the electrolysis of molten sodium chloride, the time required to produce 0.10 mol of chlorine gas using a current of 3 amperes is
(a) 55 min. (b) 110 min. (c) 220 min. (d) 330 min.

6. How many electrons can fit in the orbital for which $n = 3$ and $l = 1$?
(a) 2 (b) 6 (c) 10 (d) 14

7. For a sample of perfect gas when its pressure is changed isothermally from p_i to p_f, the entropy change is given by
(a) $\Delta S = nR \ln\left(\frac{p_f}{p_i}\right)$ (b) $\Delta S = nR \ln\left(\frac{p_i}{p_f}\right)$
(c) $\Delta S = nRT \ln\left(\frac{p_f}{p_i}\right)$ (d) $\Delta S = RT \ln\left(\frac{p_i}{p_f}\right)$

8. The van't Hoff factor (i) for a dilute aqueous solution of the strong electrolyte barium hydroxide is
(a) 0 (b) 1 (c) 2 (d) 3

9. The percentage of pyridine (C_5H_5N) that forms pyridinium ion ($C_5H_5N^+H$) in a 0.10 M aqueous pyridine solution (K_b for $C_5H_5N = 1.7 \times 10^{-9}$) is
(a) 0.0060% (b) 0.013% (c) 0.77% (d) 1.6%

10. In calcium fluoride, having the fluorite structure, the coordination numbers for calcium ion (Ca^{2+}) and fluoride ion (F^-) are
(a) 4 and 2 (b) 6 and 6 (c) 8 and 4 (d) 4 and 8

11. If the E°_{cell} for a given reaction has a negative value, which of the following gives the correct relationships for the values of ΔG° and K_{eq} ?

(a) $\Delta G^\circ > 0; K_{eq} < 1$ (b) $\Delta G^\circ > 0; K_{eq} > 1$
(c) $\Delta G^\circ < 0; K_{eq} > 1$ (d) $\Delta G^\circ < 0; K_{eq} < 1$

12. Which one of the following is incorrect for ideal solution?
(a) $\Delta H_{mix} = 0$ (b) $\Delta U_{mix} = 0$
(c) $\Delta P = P_{obs} - P_{\text{calculated by Raoult's law}} = 0$
(d) $\Delta G_{mix} = 0$

13. The solubility of $AgCl_{(s)}$ with solubility product 1.6×10^{-10} in 0.1 M NaCl solution would be
(a) 1.26×10^{-5} M (b) 1.6×10^{-9} M
(c) 1.6×10^{-11} M (d) zero.

14. Suppose the elements X and Y combine to form two compounds XY_2 and X_3Y_2. When 0.1 mole of XY_2 weighs 10 g and 0.05 mole of X_3Y_2 weighs 9 g, the atomic weights of X and Y are
(a) 40, 30 (b) 60, 40 (c) 20, 30 (d) 30, 20

15. The number of electrons delivered at the cathode during electrolysis by a current of 1 ampere in 60 seconds is (charge on electron = 1.60×10^{-19} C)
(a) 6×10^{23} (b) 6×10^{20}
(c) 3.75×10^{20} (d) 7.48×10^{23}

16. Boric acid is an acid because its molecule
(a) contains replaceable H^+ ion
(b) gives up a proton
(c) accepts OH^- from water releasing proton
(d) combines with proton from water molecule.

17. AlF_3 is soluble in HF only in presence of KF. It is due to the formation of
(a) $K_3[AlF_3H_3]$ (b) $K_3[AlF_6]$
(c) AlH_3 (d) $K[AlF_3H]$

18. Zinc can be coated on iron to produce galvanized iron but the reverse is not possible. It is because
(a) zinc is lighter than iron
(b) zinc has lower melting point than iron
(c) zinc has lower negative electrode potential than iron
(d) zinc has higher negative electrode potential than iron.

19. The suspension of slaked lime in water is known as
(a) lime water (b) quick lime
(c) milk of lime
(d) aqueous solution of slaked lime.

20. The hybridizations of atomic orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ respectively are
(a) sp, sp^3 and sp^2 (b) sp^2, sp^3 and sp
(c) sp, sp^2 and sp^3 (d) sp^2, sp and sp^3

21. Which of the following fluoro-compounds is most likely to behave as a Lewis base?
(a) BF_3 (b) PF_3 (c) CF_4 (d) SiF_4

22. Which of the following pairs of ions is isoelectronic and isostructural?
(a) CO_3^{2-}, NO_3^- (b) ClO_3^-, CO_3^{2-}
(c) SO_3^{2-}, NO_3^- (d) ClO_3^-, SO_3^{2-}

23. In context with beryllium, which one of the following statements is incorrect?
(a) It is rendered passive by nitric acid.
(b) It forms Be_2C.
(c) Its salts rarely hydrolyze.
(d) Its hydride is electron-deficient and polymeric.

24. Hot concentrated sulphuric acid is a moderately strong oxidizing agent. Which of the following reactions does not show oxidizing behaviour?
(a) $Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$
(b) $S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$
(c) $C + 2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O$
(d) $CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$

25. Which of the following pairs of d-orbitals will have electron density along the axes?
(a) d_{z^2}, d_{xz} (b) d_{xz}, d_{yz}
(c) $d_{z^2}, d_{x^2-y^2}$ (d) $d_{xy}, d_{x^2-y^2}$

26. The correct geometry and hybridization for XeF_4 are
(a) octahedral, sp^3d^2
(b) trigonal bipyramidal, sp^3d
(c) planar triangle, sp^3d^3
(d) square planar, sp^3d^2.

27. Among the following, which one is a wrong statement?
(a) PH_5 and $BiCl_5$ do not exist.
(b) $p\pi$-$d\pi$ bonds are present in SO_2.
(c) SeF_4 and CH_4 have same shape.
(d) I_3^+ has bent geometry.

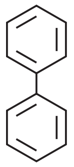
28. The correct increasing order of *trans*-effect of the following species is
(a) $NH_3 > CN^- > Br^- > C_6H_5^-$
(b) $CN^- > C_6H_5^- > Br^- > NH_3$
(c) $Br^- > CN^- > NH_3 > C_6H_5^-$
(d) $CN^- > Br^- > C_6H_5^- > NH_3$

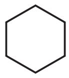
29. Which one of the following statements related to lanthanons is incorrect?
(a) Europium shows +2 oxidation state.
(b) The basicity decreases as the ionic radius decreases from Pr to Lu.
(c) All the lanthanons are much more reactive than aluminium.
(d) Ce(+4) solutions are widely used as oxidizing agent in volumetric analysis.

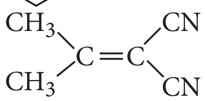
30. Jahn-Teller effect is not observed in high spin complexes of
(a) d^7 (b) d^8 (c) d^4 (d) d^9

31. Which of the following can be used as the halide component for Friedel–Crafts reaction?
(a) Chlorobenzene (b) Bromobenzene
(c) Chloroethene (d) Isopropyl chloride

32. In which of the following molecules, all atoms are coplanar?

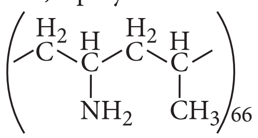
(a) 

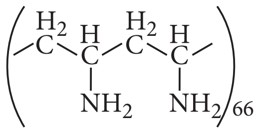
(b) 

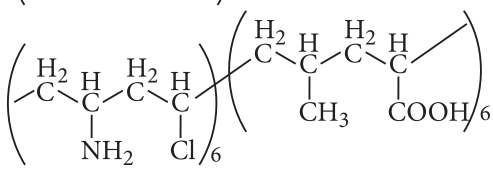
(c) 

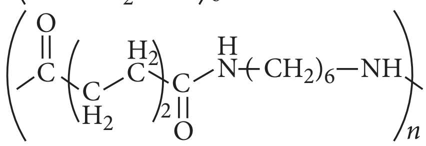
(d) 

33. Which one of the following structures represents nylon 6, 6 polymer?

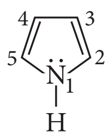
(a) 

(b) 

(c) 

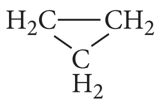
(d) 

34. In pyrrole the electron density is maximum on



(a) 2 and 3 (b) 3 and 4
(c) 2 and 4 (d) 2 and 5

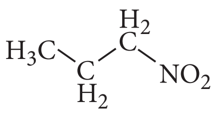
35. Which of the following compounds shall not produce propene by reaction with HBr followed by elimination or direct only elimination reaction?

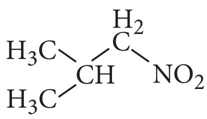
(a) 

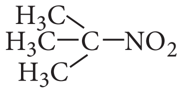
(b) $H_3C-\overset{H_2}{C}-CH_2OH$

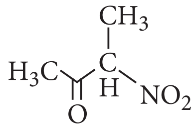
(c) $H_2C{=}C{=}O$ (d) $H_3C-\overset{H_2}{C}-CH_2Br$

36. Which one of the following nitro-compounds does not react with nitrous acid?

(a) 

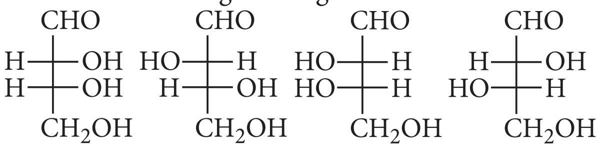
(b) 

(c) 

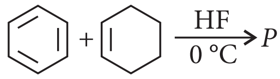
(d) 

37. The central dogma of molecular genetics states that the genetic information flows from
(a) Amino acids $\longrightarrow$ Proteins $\longrightarrow$ DNA
(b) DNA $\longrightarrow$ Carbohydrates $\longrightarrow$ Proteins
(c) DNA $\longrightarrow$ RNA $\longrightarrow$ Proteins
(d) DNA $\longrightarrow$ RNA $\longrightarrow$ Carbohydrates

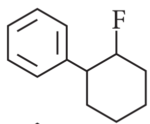
38. The correct corresponding order of names of four aldoses with configuration given below

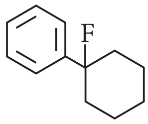


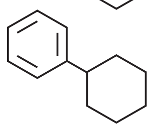
respectively, is
(a) *L*-erythrose, *L*-threose, *L*-erythrose, *D*-threose
(b) *D*-threose, *D*-erythrose, *L*-threose, *L*-erythrose
(c) *L*-erythrose, *L*-threose, *D*-erythrose, *D*-threose
(d) *D*-erythrose, *D*-threose, *L*-erythrose, *L*-threose.

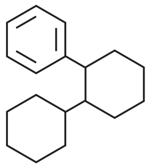
39. In the given reaction, 

the product *P* is

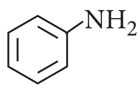
(a) 

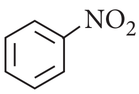
(b) 

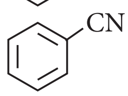
(c) 

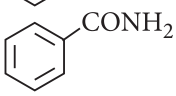
(d) 

40. A given nitrogen-containing aromatic compound '*A*' reacts with Sn/HCl, followed by HNO_2 to give an unstable compound '*B*'. '*B*', on treatment with phenol, forms a beautiful coloured compound '*C*' with the molecular formula $C_{12}H_{10}N_2O$. The structure of compound '*A*' is

(a) 

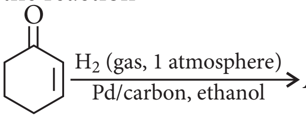
(b) 

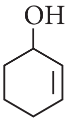
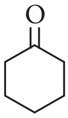
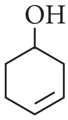
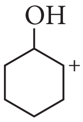
(c) 

(d) 

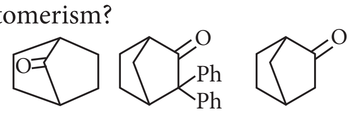
41. Consider the reaction,
$CH_3CH_2CH_2Br + NaCN \longrightarrow CH_3CH_2CH_2CN + NaBr$
This reaction will be the fastest in
(a) ethanol (b) methanol
(c) *N*, *N*′-dimethylformamide (DMF)
(d) water.

42. The correct structure of the product 'A' formed in the reaction

 A is

(a)  (b)  (c)  (d) 

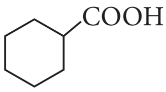
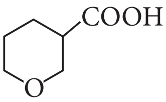
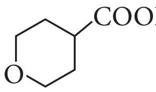
43. Which among the given molecules can exhibit tautomerism?



I II III

(a) III only (b) Both I and III
(c) Both I and II (d) Both II and III

44. The correct order of strengths of the carboxylic acids

   is

I II III

(a) I > II > III (b) II > III > I
(c) III > II > I (d) II > I > III

45. The compound that will react most readily with gaseous bromine has the formula

(a) C_3H_6 (b) C_2H_2 (c) C_4H_{10} (d) C_2H_4

SOLUTIONS

1. (c) **2.** (b)

3. **(a):** At low pressure, rate is proportional to the surface coverage and is of first order while at high pressure, it follows zero order kinetics due to complete coverage of surface area.

4. **(c):** Coagulating power $\propto \dfrac{1}{\text{Coagulation value}}$

So, the correct order is : $\underset{(III)}{MgSO_4} > \underset{(II)}{BaCl_2} > \underset{(I)}{NaCl}$

5. **(b):** During the electrolysis of molten sodium chloride,

At cathode : $2Na^+ + 2e^- \longrightarrow 2Na$

At anode : $2Cl^- \longrightarrow Cl_2 + 2e^-$

Net reaction : $2Na^+ + 2Cl^- \longrightarrow 2Na + Cl_2$

According to Faraday's first law of electrolysis,

$$w = Z \times I \times t \Rightarrow w = \frac{E}{96500} \times I \times t$$

No. of moles of Cl_2 gas $\times$ Mol. wt. of Cl_2 gas

$$= \frac{\text{Eq. wt. of } Cl_2 \text{ gas} \times I \times t}{96500}$$

$$0.10 \times 71 = \frac{35.5 \times 3 \times t}{96500} \Rightarrow t = \frac{0.10 \times 71 \times 96500}{35.5 \times 3}$$

$= 6433.33$ sec

$$t = \frac{6433.33}{60} \text{ min} = 107.22 \text{ min} \approx 110 \text{ min}$$

6. **(a):** For $n = 3$ and $l = 1$, the subshell is $3p$ and a particular $3p$ orbital can accommodate only 2 electrons.

7. **(b):** For an ideal gas undergoing reversible expansion, when temperature changes from T_i to T_f and pressure changes from P_i to P_f,

$$\Delta S = nC_p \ln \frac{T_f}{T_i} + nR \ln \frac{P_i}{P_f}$$

For an isothermal process, $T_i = T_f$ so, $\ln 1 = 0$

$$\therefore \quad \Delta S = nR \ln \frac{P_i}{P_f}$$

8. **(d)**

9. **(b):** $\underset{0.10\ M}{C_5H_5N} + H_2O \rightleftharpoons C_5H_5\overset{+}{N}H + OH^-$

$$\alpha = \sqrt{\frac{K_b}{C}} = \sqrt{\frac{1.7 \times 10^{-9}}{0.10}} = 1.30 \times 10^{-4}$$

$\therefore$ Percentage of pyridine that forms pyridinium ion $= 1.30 \times 10^{-4} \times 100 = 0.013\%$

10. **(c)**

11. **(a):** $\Delta G° = -nFE°_{cell}$

If $E°_{cell} = -$ ve then $\Delta G° = +$ve *i.e.;* $\Delta G° > 0$.

$\Delta G° = -nRT \log K_{eq}$

For $\Delta G° = +$ve, $K_{eq} = -$ve *i.e.,* $K_{eq} < 1$.

12. **(d)**

13. **(b):** Let s be the solubility of AgCl in moles per litre.

$$\underset{s}{AgCl_{(aq)}} \rightleftharpoons \underset{s}{Ag^+_{(aq)}} + \underset{(s+0.1)}{Cl^-_{(aq)}}$$

($\because$ 0.1 M NaCl solution also provides 0.1 M Cl^- ion)

$K_{sp} = [Ag^+]\,[Cl^-]$

$1.6 \times 10^{-10} = s(s + 0.1)$

$1.6 \times 10^{-10} = s(0.1)$ ($\because$ $s <<<< 0.1$)

$$s = \frac{1.6 \times 10^{-10}}{0.1} = 1.6 \times 10^{-9}\,M$$

14. **(a):** Let atomic weight of element X is x and that of element Y is y.

For XY_2, $n = \dfrac{w}{\text{Mol. wt.}} \Rightarrow 0.1 = \dfrac{10}{x + 2y}$

$x + 2y = \dfrac{10}{0.1} = 100$ ...(i)

For X_3Y_2, $n = \dfrac{w}{\text{Mol. wt.}} \Rightarrow 0.05 = \dfrac{9}{3x + 2y}$

$$3x + 2y = \frac{9}{0.05} = 180 \qquad \text{...(ii)}$$

On solving equations (i) and (ii), we get

$y = 30 \Rightarrow x + 2(30) = 100$

$x = 100 - 60 = 40$

15. (c) **16. (c)**

17. (b): AlF_3 is insoluble in anhydrous HF because the F^- ions are not available in hydrogen bonded HF but, it becomes soluble in presence of little amount of KF due to formation of complex, $K_3[AlF_6]$

$$AlF_3 + 3KF \longrightarrow K_3[AlF_6]$$

18. (d) **19. (c)** **20. (c)**

21. (b): $BF_3 \longrightarrow$ Lewis acid (incomplete octet)

$PF_3 \longrightarrow$ Lewis base (presence of lone pair on P-atom)

$CF_4 \longrightarrow$ Complete octet

$SiF_4 \longrightarrow$ Lewis acid (empty *d*-orbital in Si-atom)

22. (a, d) **23. (c)**

24. (d): $CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$

Here, the oxidation state of every atom remains the same so, it is not a redox reaction.

25. (c) : $d_{x^2-y^2}$ and d_{z^2} orbitals have electron density along the axes while d_{xy}, d_{yz} and d_{xz} orbitals have electron density inbetween the axes.

26. (a) **27. (c)**

28. (b): The intensity of the trans-effect (as measured by the increase in rate of substitution of the *trans* ligand follows the sequence :

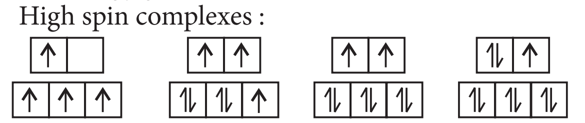
$$CN^- > C_6H_5^- > Br^- > NH_3$$

29. (c) : The first few members of the lanthanoid series are quite reactive, almost like calcium. However, with increasing atomic number, their behaviour becomes similar to that of aluminium.

30. (b): Jahn–Teller distortion is usually significant for asymmetrically occupied e_g orbitals since they are directed towards the ligands and the energy gain is considerably more.

In case of unevenly occupied t_{2g} orbitals, the Jahn–Teller distortion is very weak since the t_{2g} set does not point directly at the ligands and therefore, the energy gain is much less.

High spin complexes :



d^4, unsymmetrical d^7, unsymmetrical d^8, symmetrical d^9, unsymmetrical

31. (d)

32. (a): Biphenyl is coplanar as all C-atoms are sp^2 hybridised.

33. (d)

34. (d): Pyrrole has maximum electron density on 2 and 5. It generally reacts with electrophiles at the C-2 or C-5 due to the highest degree of stability of the protonated intermediate.

35. (c) : $H_2C{-}CH_2{-}CH_2$ (cyclopropane) $\xrightarrow{HBr} CH_3CH_2CH_2Br \xrightarrow{\text{Elimination}} H_3CCH{=}CH_2$

$CH_3CH_2CH_2OH \xrightarrow{HBr} \xrightarrow{\text{Elimination}} H_3CCH{=}CH_2$

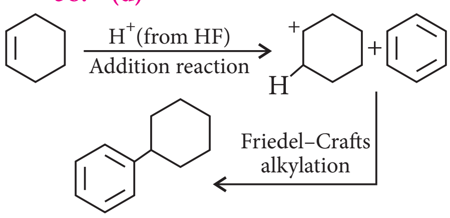
$CH_2{=}C{=}O \xrightarrow{HBr} H_2C{=}C(Br){-}OH \rightleftharpoons H_3C{-}C(=O){-}Br$

$CH_3CH_2CH_2Br \xrightarrow{\text{Elimination}} CH_3CH{=}CH_2$

36. (c) : Tertiary nitroalkanes do not react with nitrous acid as they do not contain α-hydrogen atom.

37. (c) **38. (d)**

39. (c) :



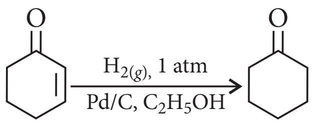
40. (b)

41. (c) : The reaction,

$CH_3CH_2CH_2Br + NaCN \rightarrow CH_3CH_2CH_2CN + NaBr$

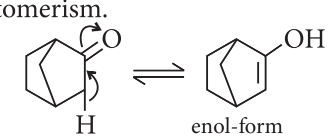
follows S_N2 mechanism which is favoured by polar aprotic solvent *i.e.*, *N*, *N*′– dimethylformamide (DMF), $H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}N(CH_3)_2$.

42. (b):



C=C bond is reduced faster than C=O bond with H_2(Pd—C).

43. (a) : α-Hydrogen at bridge carbon never participates in tautomerism. Thus, only (III) exhibits tautomerism.



keto-form (III) enol-form

44. (b): Acidic strength ∝ – *I* effect

As oxygen is more electron withdrawing (II) and (III) shows greater – *I* effect than (I). Thus, (I) is least acidic. Out of (II) and (III), (II) is more acidic than (III) as distance of O -increases from —COOH group, acidic strength decreases.

45. (a)

For detailed solutions refer to :
MTG 29 years NEET Chapterwise Solutions, NEET Explorer, NEET Guide

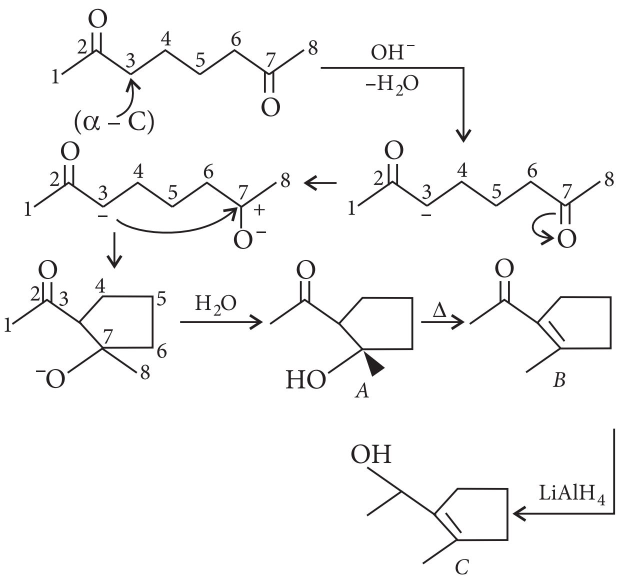
CHEMISTRY MUSING

SOLUTION SET 37

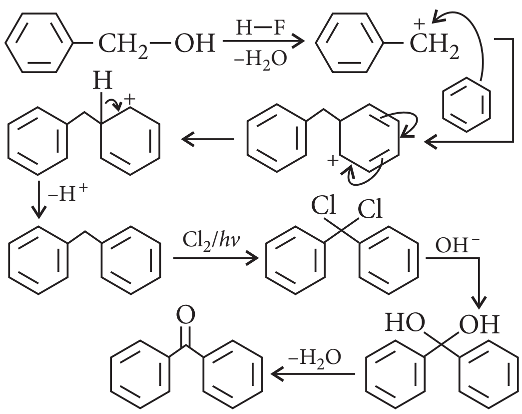
1. (c) : (c) is correct because it is conjugated diene and resonance stabilized.
(a) and (b) are not correct answers because they are isolated diene, therefore their heats of hydrogenation should be double *i.e.* 252 kJ mol^{-1}.
(d) is not correct because it is cummulative diene.

2. (a) **3. (c)**

4. (b) : Given reactant, a diketone, can undergo internal aldol condensation reaction to form *A*.



5. (c) :



6. (c) : The specific activity of a radioactive nucleus is its activity of disintegration rate per gram of specimen.

1 g of ^{31}P has $\frac{N}{31}$ atoms of ^{31}P

Thus, amount of ^{32}P in 1 g specimen = $\frac{N}{31 \times 10^6}$ atoms of ^{32}P. Thus, rate = $\lambda \cdot N$

$$= \frac{0.693}{14.3 \times 24 \times 60 \times 60} \times \frac{N}{31 \times 10^6}$$

$$= \frac{0.693 \times 6.023 \times 10^{23}}{14.3 \times 24 \times 60 \times 60 \times 31 \times 10^6}$$

Rate = 1.09×10^{10} dps per g specimen

or specific activity = 1.09×10^{10} dps per g

$$= \frac{1.09 \times 10^{10}}{3.7 \times 10^{10}} \text{ curie per g} = 0.295 \text{ Ci per g}$$

7. (d) : $\underset{(X)}{BaS} + 2CH_3COOH \longrightarrow \underset{(S)}{Ba(CH_3COO)_2} + \underset{(G)}{H_2S\uparrow}$

$Ba(CH_3COO)_2 + Na_2SO_4 \longrightarrow \underset{\text{White ppt.}}{BaSO_4\downarrow} + 2CH_3COONa$

$Ba(CH_3COO)_2 + 2NaCl \longrightarrow$ No ppt.

$BaS + BaSO_4 \xrightarrow{\Delta} 2BaO + \underset{(G')}{2SO_2\uparrow}$

$\underset{(Aq.)}{SO_2} + 2H_2S \longrightarrow \underset{\text{(Yellowish White turbidity)}}{3S} + 3H_2O$

8. (b) : $Ba(CH_3COO)_2 + K_2CrO_4 \longrightarrow BaCrO_4\downarrow + 2CH_3COOK$

9. (5) : Let the normality of BOH be *n*.
milli-equivalent of BOH = 40*n*.
On the addition of 5 mL of 0.1 N HCl into BOH solution,
milli-equivalent of HCl = 0.1 × 5 = 0.5
milli-equivalent of salt formed = 0.5
milli-equivalent of BOH used = 0.5
∴ milli-equivalent of remaining BOH = (40*n* – 0.5).
Applying Henderson's equation,

$$pOH = pK_b + \log\frac{[\text{salt}]}{[\text{base}]}$$

$$(14 - 10.04) = pK_b + \log\left(\frac{0.5}{40n - 0.5}\right) \quad ...(1)$$

Similarly, of the addition of 20 mL of HCl,

$$(14 - 9.14) = pK_b + \log\left(\frac{2}{40n - 2}\right) \quad ...(2)$$

Substracting equation (1) from (2), we get, $n = 0.088$
Substituting *n* in (1), we get, $pK_b = 4.7410$
∴ $-\log K_b = 4.7410$ or $\log K_b = -4.7412$
Taking antilog, $K_b = 1.8155 \times 10^{-5}$

10. (3) : Ethers with α-hydrogen can give ether peroxide on oxidation with air.

ANSWER KEY

1.	(a)	**2.**	(b)	**3.**	(b)	**4.**	(c)	**5.**	(c)
6.	(d)	**7.**	(c)	**8.**	(d)	**9.**	(d)	**10.**	(d)
11.	(d)	**12.**	(c)	**13.**	(c)	**14.**	(c)	**15.**	(c)
16.	(b)	**17.**	(d)	**18.**	(a)	**19.**	(d)	**20.**	(b,d)
21.	(a,b,d)	**22.**	(a,b)	**23.**	(a,b,c)	**24.**	(2)	**25.**	(4)
26.	(5)	**27.**	(c)	**28.**	(b)	**29.**	(a)	**30.**	(d)

CROSSWORD

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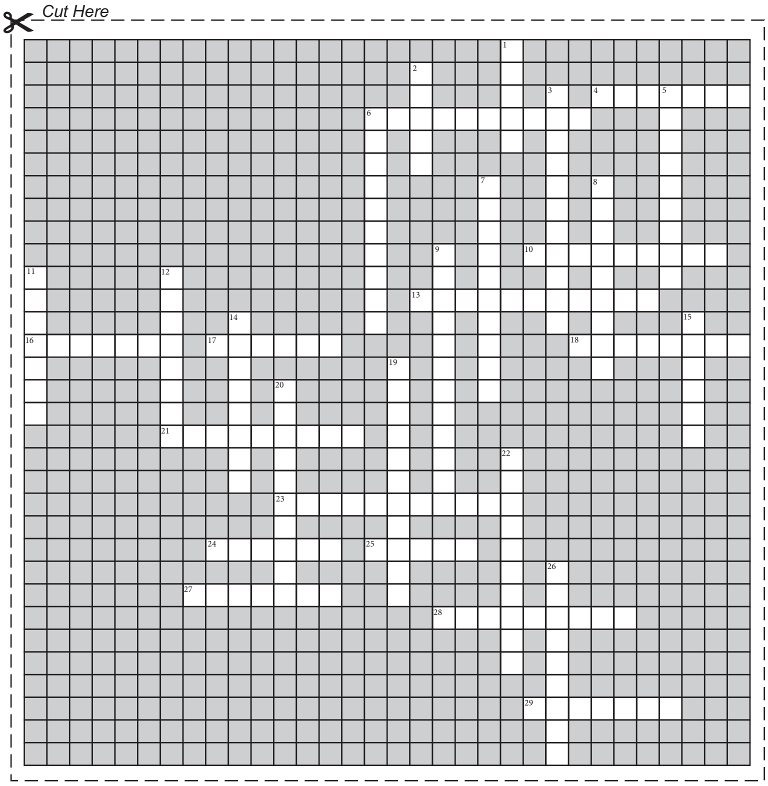

ACROSS

4. The amount of energy not available for work in a closed thermodynamic system. (7)
6. ______ acid is an acidulant added to cola drinks. (10)
10. The process of separation of two gases on the basis of their different rates of diffusion due to difference in their densities. (9)
13. Group of soluble proteins that transport fat or other lipids in the blood plasma. (11).
16. A form of carbon black prepared by pyrolysis of ethyne. (7)
17. A dilute solution of sodium or calcium hypochlorite which kills bacteria. (6)
18. Synthetic zeolite used for water softening. (8)
21. Commercial name of calcium cyanamide. (9)
23. A device for measuring volume change. (11)
24. Cross-linked phenolic polymers. (6)
25. The trivial name for diethylene glycol. (5)
27. Reagent used for carbonylation of alkyl halides. (7)
28. A reaction which consumes free energy. (9)
29. A radioisotope of hydrogen with two neutrons and one proton in its nucleus. (7)

DOWN

1. Sub-atomic particle with integral or zero spin angular momentum. (5)
2. A carbohydrate with two carbon atoms. (5)
3. Process of a solute dissolving in a solvent. (11)
5. Best known trisaccharide, composed of galactose, glucose and fructose. (9)
6. A reaction in which electrons move in a single synchronous step. (10)
7. Electrons in *d* or *f* subshells which are outside the noble gas core. (10)
8. An instrument that measures the intensity of radiant energy by employing a thermally sensitive electrical resistor. (9)
9. Compound used to stop bleaching action in paper-making industry. (12)
11. Element used as a liquid in barometers. (7)
12. Protein found in egg yolk. (8)
14. _______ was historically used as an anti-freeze for automotive applications. (8)
15. A colourless gas which when pure has a pleasant smell. (6)
19. An important non-adrenergic, non-cholinergic neurotransmitter in various parts of gastrointestinal tract. (11)
20. Element used in X-ray tubes for production of X-rays. (10)
22. Substances that are liable to ignite spontaneously on exposure to air. (10)
26. Molecules that can be converted from achiral to chiral form in a single step are known as _______ (9)

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